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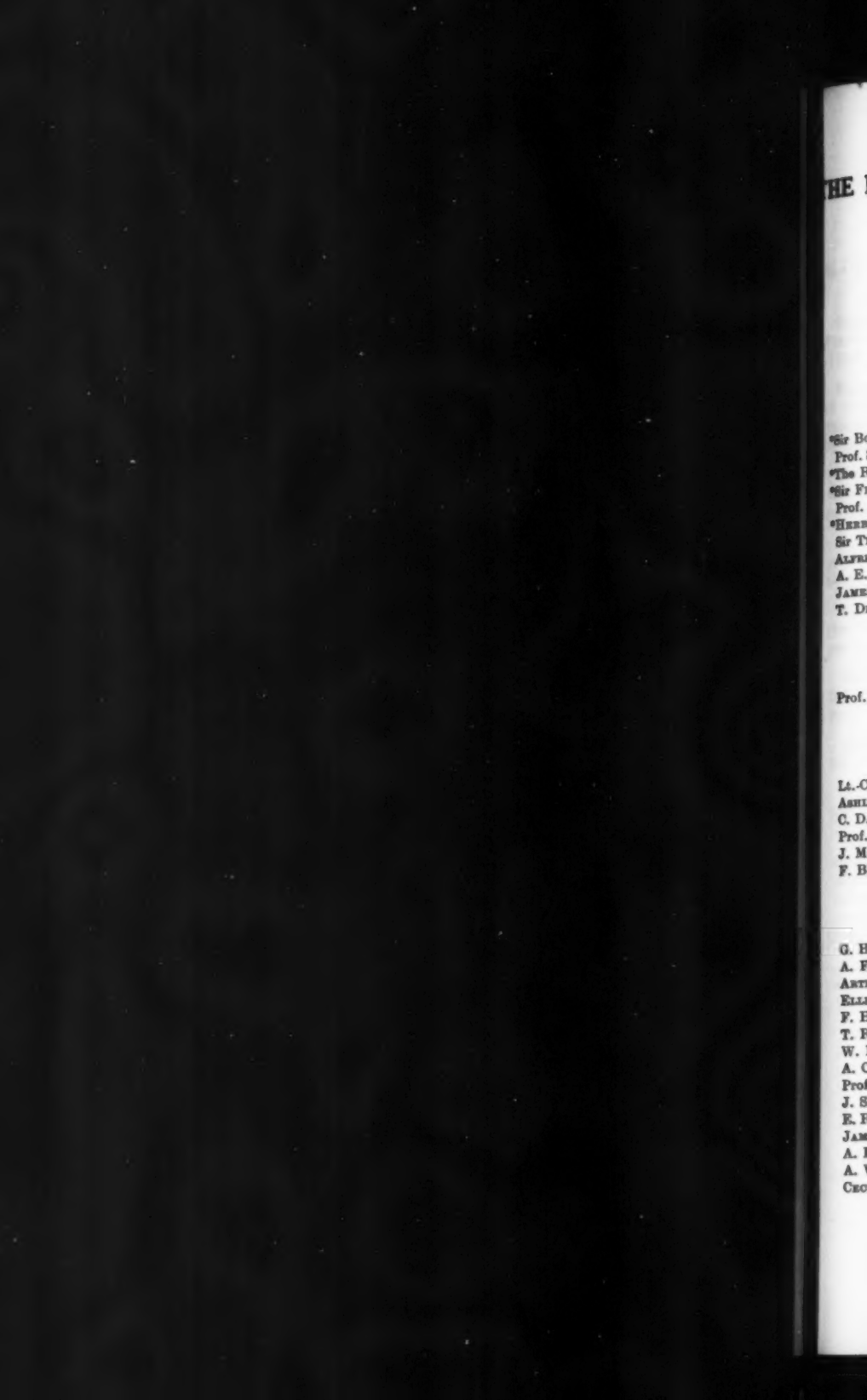

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The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

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In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 9.30 a.m. and 5 p.m. daily. (Saturdays, 9.30 a.m. to 12 noon.)

NOMINATIONS FOR MEMBERSHIP.

The following nominations for membership of the Institution of Petroleum Technologists were approved by the Election Committee on the 31st May, 1935, and the application forms may be seen at the offices of the Institution. The names of the Proposer and Seconder are given in parentheses.

As Members.

ADLINGTON, Reginald Ernest, Engineer, c/o Anglo-Persian Oil Co., Ltd., Abadan, Iran Gulf. (W. C. Mitchell; A. E. Dunstan.)

HUCH, Victor, Engineer, Str. Mecet No. 24, Bucarest, Rumania. (I. Edeleanu; P. R. Clark.)

As Transfer to Member.

HENRY, John, Engineer, c/o Compania Petrolera Lobitos, Lobitos, Peru. (J. W. Burford; G. C. Maclaran.)

As Associate Members.

MUNCASTER, Thomas Woodthorpe, Engineer, Anglo-Persian Oil Co., Ltd., Abadan, Iran Gulf. (S. Nicol; A. Reid.)

PERRY, Robert George, Geologist, c/o Kern Trinidad Oilfield Ltd., P.O. Box 55, San Fernando, Trinidad, B.W.I. (M. A. ap Rhys Pryce; C. Capito.)

As Student.

TIRATSOO, Eric Neshan, Student, Royal School of Mines, South Kensington, S.W. 7. (V. C. Illing.)

APPLICATION FORMS FOR ADMISSION.

The Council desire to direct the attention of members who Propose or Second an Application Form for admission to the Institution to the importance of sending a covering letter for the guidance of the Election Committee.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary for insertion under this heading.

Mr. W. E. D. COLE is home from Iraq.

Mr. T. W. DAGG has returned from Trinidad.

Mr. A. E. DAY is home on leave from Burma.

Mr. A. E. DUCK is home from the Punjab.

Mr. H. S. GARLICK has left for the U.S.A.

Mr. A. J. GOODMAN is now in Trinidad.

Dr. W. HOPE HENDERSON has left for South America.

Dr. J. A. L. HENDERSON is in Canada.

Mr. B. R. JACKSON is now in England.

Mr. A. N. LUCIE-SMITH has returned to Venezuela.

Mr. H. H. MARTIN has left for Ecuador.

Mr. R. H. MITCHELL has returned to the Gold Coast.

Mr. W. W. PEARCE is home from Burma.

Mr. J. G. SMILLIE has returned from Venezuela.

Mr. G. E. STOTT is returning home from Madeira.

Mr. G. S. URQUHART has returned to Assam.

Mr. C. J. WARD is home from the U.S.A.

The Secretary would be glad to learn of the addresses of the following members: J. M. Brown, R. W. Farmborough, M. Jawad Jafar, J. C. Jones, P. B. M. Linton, A. MacLean, W. J. Reynolds, W. McKechnie Robson, C. A. Sansom, K. A. Spearing, H. C. G. Vincent, and A. C. Vivian.

BURMA BRANCH.

The Third Ordinary General Meeting of the Burma Branch was held on 10th May, 1935, when Mr. A. Reid, A.M.Inst.P.T., delivered a Paper dealing with "Some Chemical and Physical Considerations Involved in the Cementing of Oil Wells." This meeting was well attended, and a most interesting discussion followed the presentation of the Paper.

Messrs. E. Procter, H. C. Carter, J. S. Pirie, and D. C. P. Phelips are at present serving on the Committee during the temporary absences of Messrs. G. W. Lepper, J. L. Benard, T. J. F. Armstrong and E. J. Bradshaw respectively. Dr. A. W. G. Bleek kindly officiated as a Member of the Committee during the absence of Mr. W. E. V. Abraham, Mr. E. Procter acting as Deputy Chairman during this period.

The Branch now has a membership of eighty.

AUGUST HOLIDAYS.

The Institution Offices and Library will be closed from 5 p.m. on Friday, 2nd August, to 9.30 a.m. on Wednesday, 7th August.

ARTHUR W. EASTLAKE.
Honorary Secretary.

"STANDARD METHODS FOR TESTING PETROLEUM AND ITS PRODUCTS."

The third edition of the Institution's handbook on the methods for testing petroleum and its products has just been published. Since the publication of the second edition in 1929 the Chemical Standardization Committee has been actively engaged in consideration of the existing methods and in the investigation of new methods for specific tests. The results of this work are incorporated in the new edition, which contains nearly 100 pages more than the previous book. Among the new tests are those for Greases (Ash, Consistency, Drop Point, Free Alkali and Acid), Knock-Rating, Existent and Potential Gum in Motor Fuels, Cold Test of Motor Fuels, Dilution of Crankcase Oil, Vapour Pressure, Tests for Liquid Asphaltic Bitumen, and Viscosity in Kinematic Units.

The opportunity has been taken to rearrange the various tests in alphabetical order in preference to classification under products, in order to avoid the large amount of cross referencing under the old system.

A new section has been included for "Tentative" methods, and contains details of tests which are required but regarding which further experience is necessary before they can be considered as "Standard."

Copies of the book, which is bound in cloth, can be obtained from the offices of the Institution, price 7*s*. 6*d*. (To Members of the Institution, 5*s*. 0*d*.) Postage 6*d*. extra.

CHEMICAL ENGINEERING CONGRESS OF THE WORLD POWER CONFERENCE.

Arrangements are being made to hold an International Congress of Chemical Engineering in London from June 22nd to 27th, 1936. The outline of the technical programme, which can be obtained from the General Secretary, 56, Victoria Street, London, S.W. 1, is as follows :—

Section A : Chemical Engineering Projects (location, lay-out, finance, raw materials, markets, etc.).

Section B : Chemical Engineering Plant Construction (materials and standards of workmanship).

Section C : Fuel, Heat and General Problems in Chemical Engineering : (1) Selection of fuel and power ; (2) carbonization ; (3) distillation, evaporation, condensation and crystallization ; (4) treatment of gases ; (5) hydrogenation, cracking and other high pressure developments ; (6) heat exchange and heat transference ; (7) lubricants and lubrication ; (8) preparation of materials on site ; (9) disposal of effluents.

Section D: Administration and Works Organization in Chemical Engineering (education and training of a chemical engineer, costing and statistics, safety and welfare).

Section E: Trend of development in Chemical Engineering (Synthetic products, high pressure, vacuum and temperature technique).

Section F: General Aspects (the translation of semi-scale processes into commercial production).

Sir John Cadman, G.C.M.G., is a Vice-President of the Congress. Dr. A. E. Dunstan and Dr. W. R. Ormandy are members of the Organizing Committee.

Lt.-Col. S. J. M. Auld, O.B.E., represents the Institution of Petroleum Technologists on the Grand Council of the Congress. Mr. J. Kewley, Mr. W. H. Cadman and Dr. F. H. Garner are members of the Technical Committee.

OBITUARY.

D. N. Dunlop.

Mr. D. N. Dunlop, O.B.E., Chairman of the International Executive Council and of the British National Committee of the World Power Conference, died on May 30th, 1935.

Mr. Dunlop was well known in the electrical industry, and had been Director of the British Electrical and Allied Manufacturers Association since 1917. Shortly after the War he conceived the idea of a World Power Conference which should be a meeting place between scientists and engineers on the one hand, statesmen and economists on the other. On June 30th, 1934, the Prince of Wales opened the First World Power Conference in London. During the past eleven years the Second Plenary World Power Conference has been held in Berlin, and Sectional meetings in five other countries. The Institution of Petroleum Technologists has warmly supported the work of the World Power Conference since its inception.

Mr. Dunlop possessed a personality of remarkable charm. He had the greatest gift of the organizer, the gift of bringing out the best in his collaborators. He would never dictate to them, but would offer each of them the possibility of making the best use of his talents. His sincerity did much to foster that atmosphere of practical idealism most favourable for the carrying on of the work of the Conference.

CONTENTS OF AUGUST JOURNAL.

The following papers are scheduled for inclusion in the August issue of the *Journal*:

"Viscosity and Thixotropy of Drilling Muds." P. EVANS and A. REID.

"Development of Wire Rope Pumping in Rumania." P. R. CLARK and L. F. W. SCHROPP.

"Specific Dispersion as a Means for the Detection of Aromatic Rings." J. C. VLUGTER, H. I. WATERMAN and H. A. VAN WESTEN.

"Refining of a Cracked Motor Spirit." D. GLYNN JONES.

"Two Methods for the Estimation of Porosity of Limestone." W. H. THOMAS, R. A. E. CHISHOLM and A. B. CAMERON.

"Bibliography of Oil Well Cement." A. REID.

"Gas-Oil Separators." J. W. HARDY.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

SUMMER MEETING.

THE Summer Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, London, on Friday, June 21st, 1935.

The Reports on the Progress of Naphthology, 1934, as published in the May and June issues of the *Journal*, were presented for discussion.

CHEMICAL AND REFINING SECTION.

Chairman: F. B. THOLE, D.Sc., F.I.C., F.C.S.

The Chairman said that the most striking advances during the year 1934 fell under three main headings. First, there were the new methods for improving the quality of lubricating oils. There had recently appeared on the market the results of several years of careful and laborious researches. Various methods had been employed. On the one hand there were the solvent extraction processes whereby undesirable components of lubricating oils were extracted, leaving an oil markedly improved in viscosity characteristics and in stability. The subject had also been approached from another angle, the treatment in this case consisting not in taking something out of the oil, but in adding something which would inhibit the undesirable chemical actions which accompany the deterioration of oil; in other words, the use of anti-oxidants. Accompanying these methods of improvement it had been necessary to devise laboratory test methods to ascertain the extent of the improvement. For example, there had been the development of various accelerated oxidation tests, such as the Indiana test, and the growing use of the viscosity index as a means of assessing the resistance of an oil to extreme viscosity changes with temperature.

Another important line of progress was on the subject of diesel fuels. The steady extension of the use of the high-speed diesel engine, and the consequent greater demand for fuel, had resulted in much experimental work, in which the Chemical Standardization Committee of the Institution had taken an active interest. The development of laboratory engine testing, the only sound method of test applicable to diesel fuels, the examination of standards for assessing knock-rating, the development of cetene numbers and the search for alternatives to cetene, and the correlation of knock-rating with other characteristics such as aniline point, were some of the current lines of investigation in this section.

The third section was concerned with motor fuels, which could be considered under two main classes: the ordinary type of motor-car fuel and the fuel of super-high octane number in particular demand for aircraft work.

As regards motor-car fuels, the subject most studied during the year had been potential gum. The determination of actual gum was a simple and widely-used analytical method, but the estimation of potential gum was a more difficult proposition. The Institution's Standardization Sub-Committee investigating this subject had done a great deal of experimental work, and was keeping in close contact with the work of the corresponding Committee in America. There was still no settled decision as to how potential gum should be estimated, although various methods had been brought forward. One of these had been included in the new edition of the Institution's "Standard Methods," but as a "Tentative" method only, because it was not yet possible to say that it was the best. As there was a definite demand for some means of determining potential gum, it was better to have one method, even if it had to be altered at a later date, than a miscellany of different methods, for the results were at least comparable. It was hoped future research would add much to knowledge on this subject.

Another important development in ordinary motor fuels was the use of anti-oxidants to prevent gum formation. This had received a great deal of study, especially in America, but it did not appear to have been employed to any great extent in Great Britain.

As regards aircraft fuels of exceptionally high octane number, there had been a number of important researches published during the last few years. There had been the very excellent summary by Banks on the effects of tetra-ethyl lead on fuels, and the interesting work of Egloff and Ipatieff on the polymerization of propylene and butylene by phosphoric acid, whereby these substances were converted into a liquid with over 80 octane number, and a still higher octane value when used as a blending agent. Although this was not yet in commercial production, it promised to be an important product in the near future. There was also the recent production, again only on an experimental scale but possessing considerable potential importance, of pure *iso*-octane. The operations of converting *iso*butylene into *iso*-octane were simple from the chemical point of view, but not so simple from the manufacturing standpoint, and the material was, therefore, expensive at present. There was no doubt, however, that a hydrocarbon fuel of 100 octane number derived from petroleum had high potentialities.

Although these three sections constituted the main lines of development during the year 1934, there were obviously a number of extremely important developments which should not be ignored. From the point of view of Great Britain, the production of motor spirit from coal by various methods was very important. The I.C.I. plant at Billingham was making a motor spirit which could scarcely be distinguished from a normal petroleum gasoline. There were various other processes operating in Great Britain for making motor spirit from coal without employing hydrogenation processes.

Reference should also be made to the C.F.R. Committee's tests at Uniontown in July, 1934, in which the correlation of road behaviour and the C.F.R. octane rating of numerous fuels had received most comprehensive and elaborate study. The results of that work had been published very fully.

Mr. F. G. Edmed said that, regarding the question of anti-oxidants in lubricating oils, trouble had been experienced over the suitability of certain lubricating oil for a special purpose. A considerable number of anti-oxidants with various types of oil had been tried in order to find a really stable product. While anti-oxidants were useful for preserving the stability of the oil at moderate temperatures, an oil was required which would stand up for long periods at a continuous temperature of 200° F., and that had proved a problem of extraordinary difficulty. It was not so much a question of lubrication as one of preventing a compass ball-bearing from corroding or gumming up. Various processes of purifying the oil had been tried, and also the effect of the addition of different anti-oxidants, but no great success had yet been achieved. The oils had been tested at a continuous temperature of 200° F., but under that condition rather quickly lost their quality. He would be glad to know whether anyone had had experience of anti-oxidants likely to be suitable for the purpose.

Dr. F. B. Thole asked whether it would be possible to adopt prevention rather than cure and have the whole unit enclosed in an inert atmosphere.

Mr. F. G. Edmed said that he did not think that that would be possible, because the bearings would have to be renewed occasionally.

Dr. F. H. Garner suggested that there were two possible reasons for the failure; either the anti-oxidant failed because it decomposed in course of time, or else it was all used up by aidation.

Mr. F. G. Edmed thought that probably the anti-oxidant was used up. The lines on which the work had been done had been the removal of all the oxidizable substances from the oil, but that was rather difficult. An ultra-purified oil had been tried and was holding up fairly well. A big demand for a stable oil was likely to arise because the compasses would probably be used on aircraft as well as on ships, although in this case it was not such a serious question, as aircraft were not away for so long a period as ships.

Mr. A. A. Ashworth said that the oil refiner was being asked to do more than should be expected of him. In the case of diesel oils, various dopes were added to make them smooth running, and in order to get a satisfactory motor or aviation gasoline it was also necessary to use a dope. In the case of lubricating oils, an anti-oxidant must be added. Was the engineer doing all he could to meet the problem from the other side? Was it not possible to improve engine design, especially diesel engines, so that knock was reduced? At first it was said that the diesel engine would burn anything, but now special oils were demanded. As a consequence the cost of fuels had risen, and it appeared that the engineer was leaving everything to the oil refiner.

Dr. F. B. Thole said that this was a matter which arose not only with regard to petroleum, but universally. It was the old question of the projectile and the armour-plate; as soon as one improvement was

made, some alteration in design achieved greater efficiency, and at once came the demand for something still better. Such competition appeared inevitable.

Captain W. H. Cadman said that he would confine his remarks to Dr. Manning's report on coal carbonization, which as far as it went was an excellent summary of the conditions of the industry and its development during 1934.

With regard to the Knowles process, this had recently been the subject of a paper by Mr. Fisher to the Institute of Fuel, but no definite figure had been given for the yield of motor spirit. During the discussion Captain Cadman had asked what was the yield of motor spirit in the commercial plant which had been running on a large scale for many months. The reply was that it was 12 gallons, including the spirit obtained by cracking the resultant oil, a figure very different from the 30 gallons given in Dr. Manning's report.

Undue notice had been given to processes not yet in operation, whilst several which had been in operation had been omitted. For example, a commercial plant of the Salermo process had been in operation for some time by the Gas Light and Coke Company, whilst a large-scale plant, manufactured in Great Britain, was in course of erection in South Africa for the distillation of shale. The Salermo process should not be confused with the Salerni process, which was also in commercial operation in 1934, and to which much prominence had been given at the last Bituminous Coal Conference in Pittsburg. The Salerni process had been tested in the North, but had been shut down. A plant was also in operation at Queensferry, near Chester.

A semi-industrial scale plant of the Thermax Process had been in operation near Birmingham for some considerable time, testing not only various coals, but also shales and cannel coals. Reference had only been made to the Belgian plants, although a much larger plant was now operating in France.

Another process mentioned was that operated by the National Coke and Oil Company, of Cannock, Staffordshire, for the distillation of a mixture of coal and oil or tar. In order to get better benefit of the tax, it had been decided to operate on the tar residues and to use only petroleum oil for starting up. This plant had now been dismantled, and was in course of erection at Tipton on a larger scale.

The above points were mentioned in order to complete the picture and to bring the report quite up to date.

Dr. Manning, probably out of a sense of modesty, had not given full credit to the work carried out at the Fuel Research Station in connection with low-temperature carbonization. Not only had they made themselves thoroughly familiar with the process and evolved a satisfactory retort of their own, but they also had an organization to test, at the country's expense, any process as soon as it was working reasonably continuously on a sufficiently large scale. The only condition was that the report on the process should be published by H.M. Stationery Office for the benefit of all. It was important that attention should be directed to the existing machinery, whereby processes for the production of oil

from coal or any other indigenous material could be tested by the Government, and that the investing public should see that such tests were made.

Dr. F. B. Thole said that thanks were due to Captain Cadman for his expert review of this section of the Reports. As regards the Knowles process, the description of that process states that the finely-ground coal is mixed to a paste with oil or tar. The difference between oil and tar as cracking stock was well known, and it would seem that the difference between the 12 gallons quoted by Captain Cadman and the figure of 30 gallons was due to oil being used in the latter case and tar in the former.

Captain W. H. Cadman said that the 12 gallons given by Fisher was for the process as operating, in which the liquid part of the mixture was entirely of coal origin. In the case of the Seaham Harbour plant the liquid fraction was understood to be petroleum, in which case the use of oil instead of tar might have a decided influence on the yield of motor spirit.

Several speakers raised points regarding the manner in which the various reports were drawn up.

Dr. F. B. Thole, in closing the discussion, assured those who had spoken on the form of the reports that their views would receive the careful consideration of the Abstracts Sub-Committee.

GEOLOGICAL AND FIELD TECHNOLOGY SECTION.

Chairman : T. Dewhurst, A.R.C.S., F.G.S.

The Chairman extended a cordial welcome to overseas members from various oil-producing countries, whose participation in the activities of the parent Institution was limited to periods of well-earned home leave. The fresh outlook and the new facts and points of view which they were able to contribute to the discussions were much appreciated and would add greatly to the interest and value of the records of progress made during 1934.

All who had access to the *Journal* of the Institution were indebted to the Authors for their excellent reports on the year's progress in geophysics, geology, drilling, production, transportation and storage, and for valuable compilations of petroleum literature and statistics. The valuable review by Professor Illing of progress in petroleum geology would be welcomed, as he did not direct attention merely to a few individual trees, but presented the main outlines of a veritable forest of facts. Geologists present would probably agree with P. D. Trask and his collaborators that 4 to 8 per cent. of organic matter in sediments was sufficient for the generation of petroleum in commercial quantities. However, the very restricted rôle assigned by Trask to bacteria in the conversion of organic matter to petroleum would probably be unacceptable to many geologists. All

petroleum geologists would, however, have welcomed the paper by Dr. B. T. Brooks, which contained much chemical evidence for the view that petroleum was formed at temperatures which could readily be conceded on geological grounds. All members would have welcomed the favourable reference to the excellent paper on Salt Domes, written by Mr. R. V. Browne, a Student Member of the Institution.

The Report on the "Geology of the Oilfields" by Mr. S. E. Coomber, a Student Member of the Institution, recorded progress in many oil-producing countries. The hope was expressed that other geologists present would be able to give first-hand unpublished information regarding the geology of less well-known oil-fields, thus adding to the interest and value of this excellent review.

The fascinating review by Dr. Shaw of the progress of geophysics emphasized the enormous amount of scientific research which was being carried out on various geophysical methods and the ever-increasing application of the methods in prospecting for petroleum, natural gas, water and various metals. It was noteworthy that the seismic reflection method retained pride of place in prospecting for petroleum. It was not surprising that in sedimentary rocks the velocity of waves increased with depth, and also with the age of the strata, due to increasing compaction and lithification. The Report was worthy of very close study by all concerned with petroleum prospecting.

The Report by Mr. Seamark on the year's progress in drilling technique was a model of lucidity and compression of statement. Points of particular interest to which attention was directed in the Report were the importance of drilling straight holes from the point of view of the avoidance of subsequent drilling difficulties, the freeing of frozen drill-pipe and casing by the application of dilute acid and the sealing of fissures in wells with plaster of Paris in order to overcome trouble due to loss of circulation. The Chairman expressed the hope that Mr. Seamark would be able to offer some degree of encouragement to those geologists who hoped that coring in full-sized hole would in course of time supersede straight drilling with fish-tail and other bits, and thus yield the maximum amount of geological evidence from wells.

The Report by Dr. May on the progress made during the year in the accumulation of fundamental scientific data relating to the control, development and production of reservoirs was of much interest and value. It was very satisfactory that experimental data had been obtained which confirmed the belief held for some years that the conservation of the original gas in the oil of the pools was much more valuable than the subsequent repressuring of reservoirs from which gas had been too rapidly withdrawn. Expansion and consequent encroachment of edge-water with decrease of pressure within a reservoir was, of course, inevitable, but the assumption of a very high value for the compressibility of water in order to explain known cases of edge-water encroachment appeared to beg the question. It was indeed a suspicious feature of the suggested potency of this ever-present cause that it would lead to the greater difficulty of explaining why so many oil-pools, in which pressure had fallen greatly with development, showed little or no evidence of water encroachment. The subject of well spacing was an extremely difficult one, but it should

be borne in mind that wide spacing was often deliberately adopted for reasons of economy during trade depressions, and therefore we should be on our guard against confusing short period with long period economy. The readjustment of the fluid pools after a period of rest in the case of the Bellevue field, Louisiana, was of considerable interest. The discovery of scientific data relating to the conditions existing in oil-field reservoirs was of fundamental importance, although the factors involved were so numerous and their influence so difficult to estimate that the fluid pools themselves would seem to be the best laboratories for observation and experiment.

The interesting and lengthy review by Mr. Satchell of progress in production technique during 1934 dealt thoroughly with the subjects of increased oil recovery by repressuring with natural gas and air, increased oil recovery by artificial water-flooding in the Bradford field, the acid treatment of wells producing from limestone reservoirs, the care and operation of small wells of low pressure situated within the Appalachian Basin and also with subjects of a more mechanical nature, such as the design of pumping units, sucker rods, etc. The Report offered a wide field for profitable discussion.

The review by Mr. Hartley on progress during the year in the transportation and storage of petroleum recorded a considerable amount of progress on the subject of the materials used in the construction of pipe-lines, improvements in the methods of construction, the subsequent maintenance of pipe-lines, including the all-important subject of corrosion and its prevention. The Report also recorded much of interest in connection with pumping stations, natural gas transport and the construction of tanks for the storage of petroleum.

Members were again indebted to Miss Clarke for a most interesting and useful review of petroleum literature published during 1934. This Report was packed with useful information, and the bibliography alone, which occupied ten closely printed pages, testified to the amount of labour involved in its compilation. This Report was non-controversial, but its value would not thereby be overlooked nor under-estimated. Almost the same remarks apply to the report by the Associate Editor and Librarian, Mr. Sell, which is a very useful compilation of statistics relating to the world's production of crude petroleum, natural gas, asphalt and oil shale with more detailed records of production, imports, exports, etc., relating to the United States and the United Kingdom.

Although most of the Authors recorded that the year under review did not witness any spectacular advance, the reports as a whole bore eloquent testimony to the enormous amount of sound and solid work which had been accomplished during the year, and petroleum technologists could rest satisfied with the progress which has been made in all branches of the subject. It was unfortunate that the Summer Meeting followed so closely on the publication of the June number of the *Journal*, as it was desirable that those who wished to participate in the discussions should have a longer period in which to study the reports. It was therefore to be hoped that in future the Annual Summer Meetings would be held not earlier than the last Friday in June. In view of the short time available for study of the reports, they were fortunate in having with

them a number of technologists with much experience of the subjects to be discussed. They need not confine their remarks to the contents of the Progress Reports, as the introduction of additional matter which was apposite would add to the interest, value and completeness of the records of progress made during 1934.

Mr. A. Beeby Thompson said that a reader would perhaps be inclined to imagine that more valuable information would be forthcoming if greater attention had been paid in the papers to failures than to the successes. The Authors dealt essentially with successful operations in the different fields. Nevertheless, a student might possibly learn far more from accounts of the numerous failures than from a few successes, because all technologists knew perfectly well that long experimenting was often necessary before the successes that were mentioned in the papers were attained.

He referred particularly to such operations as acid treatment of wells, the use of a vacuum—which was dying out for very obvious reasons; the air, gas and water drives; and the deparaffination of wells. One of the papers contained a reference to the recent use of carbide for heating wells which had been choked by paraffin, with consequent diminution of their yield. Heating was an old device which cropped up periodically in different ways. His own experience showed that the application of heat always failed to effect permanent benefit, for while it caused some immediate increase of production, the eventual consequences were much worse. Again, a reader might wonder whether so many of the new methods introduced on oil-fields were really as beneficial as their advocates had anticipated. As a technologist, he had heard that in many fields the hasty employment of air, gas or water drives, acid treatment and so on in the fields had proved a mistake and that these were gradually being dropped in favour of the old method of pumping. There were probably very good reasons for this, as there was always a tendency at the present day to run to death every new process that came forward. This had certainly been true of air or gas-lift, which had enjoyed its first period of successful activity in the Russian fields, after which it was neglected until it was suddenly resuscitated in the U.S.A., popularized and used or abused very extensively in oil-fields all over the world.

Then again, asked Mr. Beeby Thompson, were technologists not somewhat over-impatient to get results? In their anxiety to recover the contents of oil pools quickly they were endeavouring to imitate nature by artificially reproducing her methods; and whereas she occupied tens of thousands of years in effecting concentrations of oil on structures, engineers wanted to do the same thing in the course of a few months or a year or two. He had no doubt that many of the abandoned oil-fields would be rejuvenated even if left alone, and that the oil, water and gas would gradually segregate and in time form new, if smaller, fields if the structures were securely bottled up and left undisturbed. Engineers endeavoured to secure a reconcentration of oil by applying methods which acted too quickly, and in consequence they often met with disappointment. After all, the movement of oil and water in sands depended largely on permeability, and permeability must be fairly regular for the free

movements of fluids. Sands useful for fluid drives must neither be too permeable nor too impermeable. There were very few fields in the world which could be as successfully operated as those which were at present being handled in America, such as the Bradford field. Where the water drive was most successful, the sands were exceptionally regular and constant in their permeability and their impregnation with oil.

Mr. Beeby Thompson also paid tribute to the value of the metallurgist. Unless the metallurgist had given the oil technologists metals which would withstand the hard treatment to which they were now subjected, they could never have made the headway in oil-field technique which they had achieved. As an example of the high standard of material and workmanship, the following data given by an American technologist a few days ago may be cited. He had described the pumping of a well 8500 ft. deep with a $1\frac{1}{16}$-in. pump on a 72-in. surface stroke, with double plunger and suction valves, delivering 130 barrels a day at 18 strokes per minute. This well had pumped without hindrance for nine months, a result which would have been absolutely impossible even two or three years ago. It showed the tremendous advance that had taken place in the quality of the metals used. In this particular case the efficiency was extremely high—something like 75 per cent., for the oil, it was said, was actually being raised the full 8500 ft. He particularly stressed that point because it should be noticed that the pump had not been flowing by heads, but pumping regularly at each stroke, which meant that at the bottom of the pump there was a pressure of something over 3000 lb.

He remarked that it was interesting to see a return being made to the use of wooden tanks, which were so very resistant to corrosion; and also a reference to the diminishing value due to control methods of the decline curves, which had been much used at one time by petroleum technologists for estimating the productivity and life of oil-fields.

Mr. G. W. Lepper said that in Professor Illing's review of "The Geology of Petroleum" it was stated: "It is probable that in organic content a source rock of petroleum is not vastly different from many of the ordinary marine sediments, the enrichment of the reservoir rock being mainly a question of segregation."

It was also stated that Trask and other workers associated with him in research on source rocks were impressed "with the possibilities of migration from organically rich sediments in the middle of a marine basin of deposition."

Geological evidence from Burma and Assam was, broadly speaking, in accord with these views, and it would be interesting to learn if members present who had worked in other oil-fields had been led to similar conclusions with respect to the origin of their oil accumulations.

Under the heading of "Geophysics," Dr. Shaw mentioned the Schlumberger "electrical coring" process—better termed, in Mr. Lepper's opinion, "electrical logging." During the past two years this method of recording information from the uncased bore hole had been the subject of very thorough trials in Burma and Assam, and he was able fully to endorse Dr. Shaw's statement that the method had been an outstanding success in the correlation of well logs over extensive areas. At first, very careful

comparisons had been made between the electrical logs and the data furnished by previous coring of the same or near-by holes. In this way the "resistivity and porosity" characteristics of the common lithological types had been ascertained, and the geologists had proceeded to interpret uncored but electrically logged data in lithological terms.

After a few such surveys had been made, they had been greatly impressed by the close agreement between the electrical logs of wells at considerable distances—at that time about 3000 ft.—apart. Moreover, they had found that certain "marker" beds, discovered by coring a year or two before, had shown up clearly in the electrical logs. Beyond this, a whole sequence of marker beds—usually shales—had been found to occur in the Schlumberger records. They had soon given up the practice of converting the whole of each electrical log into lithological sequences, and had made direct comparisons of the electrical records, correlating hundreds of feet in ranges over which they possessed little or no core evidence. Precise details of faults, the existence of which had been known from surface mapping or inferred from coring, had begun to be obtained, but perhaps the most surprising feature had been the proof of the existence of faults underground for which no surface outcrops had yet been found.

The interpretation of results demanded a large amount of careful detailed study of the Schlumberger logs, but the geologist was well repaid for this addition to his labours by the confidence he could place in the correlations established by this means. Nor was it all plain sailing, for one often found stretches of electrical records which did not fit in at all well with those of near-by wells. Such discrepancies were most common in the first few hundred feet from the surface; at greater depths they seldom occurred.

While the majority of the wells surveyed had been drilled by the rotary method, some success had been achieved when deepening old producers with cable tools. After careful drilling and cleaning out below casing, a hundred or more feet of open hole at a time might be surveyed electrically. Caving was, of course, the principal obstacle in this work.

They had so far been disappointed in their attempts to deduce from the Schlumberger logs whether a sand drilled through by rotary was likely to be productive. The problem was an important one, as a mistake meant the premature cementation of casing. Perhaps they had hoped for too much from what they had been told of results in other countries. It was, however, only fair to say that some useful evidence was being obtained, and that for a certain sand in particular local areas it was possible to feel fairly sure that an average resistivity of more than x units rendered a test desirable; and that, where the sand had an average resistivity of less than y units, it was almost certainly not worth testing. The appearance of the cores of the sand and their oil and water content were valuable confirmatory evidence. Wherever possible, also, a test was made without setting casing by means of some form of tester on the drill pipe.

Under the head of "Drilling," he expressed a certain disappointment at the absence of any reference to the problem of core recovery. The experience of his colleagues had been that, in general, recovery was good until critical ranges containing oil sands associated with shales and sandy shales were reached. It then often happened that recovery percentages were

low, just when full recovery was most needed. Sometimes part of the lost core was recovered in the next run, but it frequently was not. Many members had no doubt had similar experiences, and, like Mr. Lepper, hoped that a core barrel would soon be devised which would give consistently high recoveries under all conditions. Their experience was that the greatest losses occurred when cores of small diameter had to be taken in deep holes. He added that he did not wish anything he had said to be construed as a criticism of the technique of the drillers on the fields with which he was concerned; they were highly skilled men, and took great pains to get the geologists what they required.

He had been much interested, he said, to read an abstract (No. 613) in the June issue of the *Journal* referring to a new coring apparatus which, when the receiving tube was full or became plugged so that no more core could enter, indicated to the driller that he was no longer taking a core. Mr. Lepper confessed that he could not understand how this indication was brought about, but it was said to prevent the driller from drilling on into lower formations when the expansion of the first part of the core had filled the core barrel before it had drilled its full length. It had been stated that instances of core expansion had been noticed in coring with almost all types of core barrels, but that recovery was usually so imperfect that no quantitative idea would be obtained of the importance or amount of core expansion. This idea of expansion, said Mr. Lepper, although credible enough, was new to him, and he would be interested if any member present could say more about it.

Referring to Dr. May's interesting summary of progress under the heading of "Scientific Control, Development and Production of Reservoirs," he feared that, at the time he had left for the United Kingdom in March, technologists in Burma had not been able to say much about bottom-hole measurements. Experiments were being carried out with a bottom-hole temperature and pressure recorder, and with a bottom-hole fluid sample taker as opportunity permitted. Difficulties due to inexperience and to the fact that conditions at the bottom of the hole were very different from those in Iran were still being overcome. Technologists in Burma were still convinced that it was wise to produce oil at the lowest possible gas–oil ratio, and were impressed with the difficulty of restoring the dissolved gas content of crude in their sands when pressure fell.

On the subject of well spacing, the tendency in the older fields in Burma, where there were several sands to go for, was for closer rather than for wider spacing. This tendency had, with few exceptions, been justified by results. Mr. Lepper emphasized the desirability of careful directional surveys of wells in areas which had been drilled-up under a regular surface-spacing scheme. Although the up-dip rule for deviation of bore-holes held good in the general sense, it did not do so precisely, and the paths of regularly spaced wells might diverge or converge. There also existed the probability that the amount of deviation of neighbouring wells might differ considerably. It followed that a plan showing the position of each well at the oil sand level would often reveal several large gaps in the spacing in which new wells might, even at a late stage in development, be drilled with profit. The experience of technologists in Burma with such wells had been almost uniformly satisfactory.

Mr. C. A. P. Southwell observed that the three contributions from Mr. Seamark, Mr. Satchell and Dr. May had one common factor, viz. acid treatment. All had quoted the recent developments in acid treatment as a development of importance during the previous year. Whilst the recent increase in use was actually new, the practice was comparatively an old one. Mr. Southwell proposed, therefore, to say a few words on acid treatment, especially as in Mr. Satchell's report there were certain figures which he wished to discuss, which, in view of Mr. Satchell's absence abroad, he had not had the opportunity of discussing with him.

He had been interested to see in Mr. Satchell's report that the author referred to the historical side of chemical treatment. (Reference No. 2. "Livy: Histories: Punic War.") As Mr. Satchell was not present and Mr. Southwell could not ask him about this reference, he presumed that the writer referred to the famous occasion on which Hannibal had been stopped as he was crossing the Alps by a large boulder—a limestone boulder, it might be presumed—which had fallen in a narrow pass. It was stated that the Carthaginian leader had overcome this obstacle by lighting fires underneath it and pouring on, it was said, vinegar.

Dealing with the historical side as far as the actual acid treatment of wells was concerned, Mr. Southwell said that he had no information of the first occasion on which acid treatment was undertaken in wells. He assumed that the American fields provided the first occasion, but it was interesting to note that the Institution had present with it that day a member who had been responsible for the first acid treatment in Iran: Captain W. H. Cadman. This occasion was in January 1925, more than ten years ago, while Captain Cadman was in charge of chemical research in the Iran fields, and he had recommended the use of acid treatment in the loosening of a badly stuck string of cable tools. One speaker had referred to the obligation to record failures; unfortunately Mr. Southwell had to record that this attempt had not been successful, but attempts made subsequently to this one, which had been started by a member of the Institution, had met with considerable success.

One of the important points in connection with acid treatment was suggested by Mr. Satchell's remark that "research has been stimulated on problems," and Mr. Southwell wished to point out that it was absolutely essential to undertake laboratory research before acid treatment was tried out in actual practice. Samples should be taken of the wall of the hole which was going to be acid treated; representative samples should be provided by the geologists; and these should be tested with various strengths of acid. They should also be tested under different pressures to find out the effect of pressure. The question of agitation should also be investigated. To undertake this, research work on laboratory scale beforehand was necessary in order to achieve success with the first treatment and to prevent the use of an unnecessary quantity of acid.

Mr. Satchell had used some figures with which workers in Iran did not agree and which their experience did not confirm; they might represent actual experience in one field, where the type of rocks encountered might have been such as to necessitate the acid strength mentioned. He wished to refer to page 524, where it specified commercial hydrochloric acid, containing about 30 per cent. HCl by weight. The results confirmed in practice

indicated that the optimum concentration was in the neighbourhood of 16 per cent. by weight of HCl. No particular gain would be effected by increasing the concentration above this figure. It was obtained by using approximately one volume of commercial HCl to one volume of water.

Mr. Satchell had also mentioned the use of inhibitors. The general inhibitor in use was sodium arsenite. Mr. Satchell, however, said that: "By an inhibitor is meant a substance of such a nature that the addition of 10 to 15 per cent. by weight of the acid retards or prevents the attack of the acid on metals." Mr. Southwell said that his own colleagues had found that 0·5 per cent. was a suitable amount to use.

An aspect of acid treatment not mentioned in Mr. Satchell's brief review was that of safety precautions. It was very desirable that the crew who were running the acid treatment should be provided with suitable goggles, and that sodium bicarbonate should be at hand to apply immediately a leak occurred, whether it was due to a pump or a well-head fitting, so as to prevent burns. Now that acid treatment was used as a routine practice in many fields, it was rather surprising that the result of this obvious marriage of HCl and limestone had not yet reached adolescence. Even now it was still only in its infancy as far as the detailed technique was concerned. Portable chemical units had been developed for this purpose, and were used in the United States by the chemical companies who did this work, but many of the fields were adapting equipment unsatisfactory for the purpose. Yet the cost was small and the results of great economic value.

The acid treatment was used for three main purposes: first, for fishing operations, to facilitate the loosening of tools; secondly, to take off the calcareous mud skin that was found on the walls of the well; and thirdly, to improve the entrance of oil to the well by increasing the fissure size or the pore spaces. For a normal production operation in Iran fortunately very few of the wells were drilled into areas of tight limestone, and the majority of the wells drilled were more or less on a par with each other, and gave similar productivity on any one field. Occasionally, however, wells were drilled into a part of the limestone which was tight, and the well might be completed without penetrating as many fissures in the open parts of the limestone as the general run of wells, and acid treatment was tried. The normal practice was to use 500 gallons of commercial acid, and to add this quantity to 500 gallons of water, to which the inhibitor had previously been added. The next point that arose was: how long should the acid be left against the wall of the hole? and here it was necessary to consider the well pressures. As all members knew, if the pressure were increased, the chemical action was retarded. It had been found in Iran that in the majority of the cases about 60–70 hours was the usual length of time necessary, and from American publications this appeared to be about the time that was used in their fields. It was necessary to work out this time beforehand on a laboratory scale, and to adjust the result to the actual conditions.

It would, moreover, be desirable, if possible, to agitate the acid while it was against the wall of the hole. This was a difficult operation to achieve, and the difficulty was overcome by running three separate acid treatments. After the first treatment, the sludge was removed, and the well was flowed, or bailed, and the second acid treatment was undertaken. This was

followed by a third acid treatment. The three operations amounted to the same thing as agitating the acid, because it removed a film which formed on the face of the wall rock as soon as treatment started, and which delayed the action of the acid.

As an example, Mr. Southwell quoted results from a small well which had been producing at the rate of about 400 tons a day, with a bottom-hole differential of 300 lb. This well had been acid treated, and the well had then given about double the original production—about 800 tons—with a bottom-hole differential of 5 lb., which was a very great improvement upon the original 300 lb.

Another interesting problem had been presented by a well over 5000 ft. deep—a fishing problem due to a faulty tool joint. The bit and bottom length or two of the drill pipe had been left in the hole, and the top of the fish was somewhere about 5200 ft. in the well. A wash-over string with Kamerdiner jars had been run over the top of the fish. Jarring had been started, but the fish could not be moved, and it had then been decided to use acid treatment. The acid had been circulated down, but the acid used in that case had been three parts of commercial HCl to one part of water. This strength had been employed in order to get as rapid a result as possible. This acid had been pumped in by stages: 200 gallons at first, left for 45 minutes, and then succeeded by another similar quantity, and so on, with a view to increasing the agitating of the acid. After treatment had been given with about 1000 gallons of the mixture, the well had been flowed, but on circulating, the losses had been found to be of the order of 300 cu. ft. an hour. This had indicated that the acid had opened up a fissure, but the operators had not known where this was; it might have been above the fish. At all events, the acid was being lost in the rock, and was not effecting the object required, with the result that the fish could not be recovered.

A second treatment was given, but before this the well had been mudded off until the losses were only 8 cu. ft. per hour, in order to conserve the acid. The result of the second shot was that the losses rose to 2000 cu. ft. per hour, and again the fish could not be recovered.

On the third attempt the U-tube effect of the drill-pipe was taken advantage of; high pressure gas had been put on the annular space, and the fluid in the annular space pushed down several hundred feet and the acid run in until the bottom of the acid slug was at the foot of the drill pipe. The pressure was then immediately released in the annular space, with the result that the U-tube effect left the acid in contact with the fish, and it was then recovered without any trouble. This, being a deep well, was one on which a large amount of money had been spent, and the whole of that expenditure might have been completely lost had it not been for the acid treatment. As the price of 500 gallons of commercial acid and 50 lb. of inhibitor is about £100, the advantage of this practice will be readily appreciated.

Capt. W. H. Cadman observed that Mr. Satchell and Mr. Southwell had covered the question of acid treatment so thoroughly that very little remained for him to do except, possibly, to throw a little light on the cause of the failure of the first attempts at acid treatment which had been made

ten years ago in Iran. Almost in despair, he said, after trying, without any success, all the known methods of fishing for a string of tools which had been stuck in a well at Maidan-i-Naftun, the Area Superintendent at that time, Mr. W. E. D. Cole, had approached him as Director of the Research Department which the Anglo-Persian Oil Company had just established at the oil-fields, and had asked him to see whether the Chemical Department could help to loosen the tools. Knowing that the formation was largely limestone, the idea of dissolving it in dilute acid at once suggested itself, both as a possible means of helping in a fishing job, and also for the purpose of increasing production by opening up tight formations. Many factors, however, had to be taken into consideration. Some preliminary work was immediately put in hand to ascertain, if possible, the desirable strength of commercial hydrochloric acid for the purpose; the effect of the acid on the iron and steel encountered, such as the casing, etc., and how to prevent or retard this corrosive action; and also the effect on the acid of the drilling—water, gas, oil, and other things that might be met with in the well. So far as the laboratory work was concerned, he and his colleagues had rather flattered themselves that they had solved the problem, at least on the laboratory scale. The conditions, however, were by no means the same, when the process came to be applied to the well itself. He considered it necessary to mention at the outset that no inhibitor was available in Iran in sufficient quantity for treating the large volume of acid required to be put down an oil well. Sodium arsenite was not the kind of substance that might be expected to be easily obtained in any quantity when working 150 miles away from the Iranian Gulf; nor could any other satisfactory inhibitor be discovered and obtained at a moment's notice. At that time, very little, if any, work had been done on the various chemicals which can now be added to an acid in order to inhibit its attack on iron and steel. The first large-scale attempt had therefore to be made without any inhibitor.

This was the principal cause of the failure of the first attempt to use acid. Through over-cautiousness, arising from the fear of damaging the casing and pumps, etc., in the actual large-scale application, the acid used was far too dilute. As a result, the action of the acid on the limestone was much too slow to bring about the desired effect in the limited time available for the trial. Success, however, came by trying and failing, and failing and trying again. He gave great credit to the Production Department and the Fields Management for the fact that, although his first attempt at acid treatment had been unsuccessful, it was appreciated that the conditions under which the work had been done were far from satisfactory. Sodium arsenite was procured in quantity for use as an inhibitor, and the subsequent efforts at acid treatment had met with the success to which Mr. Southwell had referred, and without any damage to the casing or equipment. He was definitely of opinion that the controlled acid treatment of wells, in certain formations such as limestone or other rocks soluble in acid, would be used with advantage and profit much more extensively in the future.

Mr. P. Evans said that his few comments would refer not so much directly to the papers themselves as to a few points that had been suggested by them, more particularly by the papers of Mr. Coomber and Mr. Seamark.

He was sure that those who, like himself, were very closely concerned with actual field operations would have found Mr. Seamark's paper to be particularly suggestive. It had occurred to him that it might perhaps be of value to add some few notes about a subject that did not receive much attention in that paper: pressure drilling. Pressure drilling had been going on in Assam for some little time at one of the exploratory wells. In most cases in which pressure drilling was resorted to it was needed for perhaps the last few hundred feet of wells, or for drilling through some one particular zone; but in the well which he had in mind 3600 feet had been drilled since surface pressure had first been applied, and nearly the whole of that footage had been made under pressure in the face of a combination of drilling difficulties due to alternating hard and soft strata, very steep dips, high-pressure gas and water sands, and heaving shales scarcely to be equalled anywhere in the world. Surface pressure had varied; attempts had been made to keep it as low as possible, but it had often been necessary to hold pressures greatly exceeding 1000 lbs. per sq. in. even when using extremely heavy mud. Recently the total hydrostatic pressure at the bottom of the hole—mud weight plus back pressure—had amounted to over 7500 lb. to the square inch.

The problems of fishing under pressure were largely new ones. There was little reference in the literature to the troubles of fishing in pressure drilling, but the drillers had had to tackle them, as, owing to the heaving shales, the drill-pipe had been stuck on several occasions, and it had almost always been impossible to get circulation. Whenever possible, before tackling a fishing job, it was best to replace surface pressure by using extra heavy mud, but obviously this could be done only if the circulation was free or could be made free by a very deep back-off, or by shooting off the bottom of the pipe. In one fishing job an attempt at shooting off the bit and oversize drill-collar had been made and had been almost, but unfortunately not quite, successful; the attempt was worthy of being placed on record, as it had been, they believed, the first time that shooting had been attempted in a well drilled under pressure. Even with free circulation the surface pressure might be too high for replacement by heavy mud, and during another fishing job some of the drill-pipe was successfully cut off and extracted under pressure, and he believed that this was the first time that this had been done. At the same well, a directional survey had been made under pressure, using a multiple-reading magnetic inclinometer. The well had been drilled with a Doheny Stone equipment with certain local modifications, the driller in charge being Mr. W. C. Schmittou.

Mr. Seamark, in referring to the problems of drilling mud, had recorded the preparation of mud weighing about 155 lb. which apparently contained no ordinary clay. In India they had used muds up to about 150 lb.; these had as a basis a mixture of clay and ground shale and were loaded with barytes. With these muds it had been found that, generally speaking, waterglass had been rather more helpful than either soda ash or sodium tannate. The drillers had not found the 145 to 150-lb. mud altogether to their liking, and had expressed the desire for a light mud, by which they meant mud weighing about 130 lb. A 135-lb. mud had therefore been produced, and this had been in use for quite a few months, and seemed to have worked reasonably well.

A point of interest in Mr. Seamark's paper had been the importance of preventing caving from starting, and also of drilling slowly through the bad formation. Mr. Evans' experience has been that even if prevention of caving was a difficult matter, its cure was well-nigh impossible. They had found that very often a hole that was apt to be rather troublesome at first in the way of squeezing or heaving tended to clear up considerably after a few days' steady drilling. Reference was also made to the swabbing action due to rapid removal of the drill-pipe when it was pulled up for change of bit, and in this connection he wished to direct attention to an article by Cannon (*Oil Weekly*, 23.4.34, **73** (6), 21). This author obtained evidence to show that the reduction of hydrostatic pressure was possible at the bottom of the hole even with quite slow withdrawal of the drill-pipe, if the mud had a rather high yield value, and his paper indicated lines of inquiry which should help to reduce the risks of blow-outs and heaving during withdrawal of the drill-pipe and deserved careful study.

The remarks that Mr. Southwell had added to Mr. Seamark's paper, and to the other references to the use of acid, had been very interesting, but he, for one, would like to hear even a little more about the use of acid for freeing stuck drill-pipe, particularly in regard to the minimum amount of calcareous matter in the strata that were being drilled through. Obviously, if limestones were present, and formed a fairly large proportion of the strata, the acid treatment would have much more chance of success than with shales or mudstones which might be comparatively poor in calcareous matter. It might be very helpful to know what was the least proportion of calcareous matter present when this method of freeing drill-pipe had been successfully used.

Another point referred to in Mr. Seamark's paper had been the use of plaster of Paris. Here again, rather more detail would be useful. The only example that had come to his notice had unfortunately been unsuccessful. Plaster of Paris in quite large quantities had been used over a period of several weeks, but in the end the well had had to be abandoned.

In connection with straight drilling, the hydraulic feed and, more especially, the hydraulic table seemed to be of importance. The delicacy with which the bit could be controlled by the hydraulic table was a great aid in getting the hole straight. It seemed to Mr. Evans that it enabled gravitation to play its part. Indian experience did not altogether support Mr. Seamark's generalizations that there was little difference between the time taken in drilling crooked and straight holes. The extra time required was certainly not very great in some fields, but where drilling was more difficult, straight drilling might be very much slower, and consequently much more expensive than getting down as fast as possible, regardless of the verticality of the hole. He did not for a moment wish to suggest that it was undesirable to drill straight, but he wished to emphasize that in some areas it seemed to add greatly to the time and expense of drilling, whatever method was used for keeping a fairly straight hole. He also thought that although engineers were all agreed that it was important to detect the first signs of crookedness, it was also important to know where to start straightening a hole that had already gone off. He knew of a recent instance of the value of a closely spaced survey of such a well. The readings had been taken at intervals of 20 to 30 feet over the critical range, to find the best

spot to start a shoulder for getting into a new hole. Unless the right depth for starting a shoulder was chosen, it was a very easy matter to waste a great deal of time and money in reaming without any success. When drilling under pressure, Bettis protectors could not be used, and the risks of windowing the casing, and even the drill-pipe itself, must be much greater when the hole was crooked than when it was reasonably straight. This seemed to be an additional argument for endeavouring to keep as straight as possible in a well which was being drilled under pressure conditions.

Referring to Mr. Coomber's admirable report, a great amount of detail had been included, and it was impossible for an author with the most encyclopædic knowledge to deal fully with all the papers under review. Reference was made to the papers by Condit and Stamp on India and Burma. Those technologists who were familiar with those countries would realize that, as these two papers were written some years ago, both were in a varying degree out of date. Neither paper took into account the more recent writing, such as Mr. Lepper's paper at the World Petroleum Congress in 1933. Mr. Coomber had made a slight slip in referring to recent wells drilled in Baluchistan, evidently having been misled by the reference to that paper in Condit's paper. The annual reports of the Geological Survey of India showed that there had been no recent drilling in that province. During the year a brief but important paper had been published by Gee (*Current Science*, 1934, **2**, 460), giving his views on the Salt Range and on the age of the salt—whether it was Cambrian or Tertiary. In view of the many oilshows and the neighbouring oil-field of Khaur, this work, although not directly connected with petroleum geology, had a very important indirect connection, and was certainly of very considerable interest. He wished also to direct the attention of members to a paper by Rich (*Bull. Amer. Assoc. Petr. Geol.*, 1934, **18**, 1584) which was of interest to geologists concerned with structural problems, and which deals with problems of low-angle overthrust faulting.

Mr. Coomber referred to the use made of heavy minerals in oil-field correlation work in America. The micropetrological method had been found to be of great assistance in India, and in a normal year's working, something approaching 5000 slides of Indian Tertiaries were dealt with. It was important to use the utmost caution in applying the evidence, but with the necessary care taken to view the results broadly, correlations were possible which could scarcely be reached without petrological aid.

A reference to Bramlette's paper quoted by Mr. Coomber showed that the results of mineral analyses were very difficult to present in a readily intelligible form unless recourse was had to some graphical means of representation. From a series of columns of figures, it was almost impossible to form a mental picture. The Burmah Oil Company's experience of the past two years had amply confirmed the usefulness of the scheme of graphical representation which had been gradually developed in previous years, and had been described at the World Petroleum Congress.

Although time prevented him from giving detailed reference to other progress reports, he desired to emphasize the value that each one of these reports had in presenting a review of what had been done during the past year in the different spheres of the industry, and the great assistance that

they afforded in indicating to the men on the oil-fields where to turn for information. It usually happened that library facilities were not of the best, and it was impossible to obtain every particular reference which was noticed; moreover, a worker had not the time to hunt through a large number of publications on the off chance of finding something that would be useful.

Captain D. Comins said that he was impressed by two of the general remarks made by Mr. Beeby Thompson. One of these had been that sufficient stress was not laid upon failures in papers that were presented. This was very true. It was often not possible to appreciate the particular significance of some feature of an instrument or a process unless one also appreciated the reasons that had led up to it. As a minor illustration, he mentioned a pressure indicator which he and his colleagues had evolved in Iran some years ago, and which had since been replaced by another and different type. In this first instrument the well pressure was transmitted through a piston to an indicating device, and when first tried out it was found that a leak of gas past the piston frequently made the results useless. A seal of lubricating oil was therefore used to prevent direct contact between the reservoir crude and the piston, and successful results were obtained. The seal was thus clearly indispensable, and the best way of stressing its importance in describing the instrument was to mention the earlier failures which had led to its incorporation.

Another of Mr. Beeby Thompson's remarks with which he desired to express agreement was that in which Mr. Thompson had said that technologists should not be in too much of a hurry. It was necessary in doing their work to differentiate between geological time and productive time. The processes in the reservoirs that were theoretically quite all right did not work out in practice in the limited time during which a field had to be evacuated. This, for example, was the reason why gas dome repressuring to try to force gas back into solution was not a practical proposition. It was purely a question of time.

He now wished to refer particularly to Dr. May's paper. Anyone reading it could not fail to be impressed by the increasing amount of precise physical data that were being observed and recorded in reservoirs. In that respect it was clear that there was a certain change from the rather obstructionist opinion held some years ago that such data were useful only in certain reservoirs with free convection. For example, in recent years bottom-hole pressure measurement had become practically standard practice, and its application to proration and to reservoir control was more or less routine. Bottom-hole sampling, however, had to some extent lagged behind. Up till 1934 the only exhaustive investigations were those made by the Anglo-Persian Oil Company in Iran and by the United States Bureau of Mines (Lindsley) in East Texas. Since then, however, as could be seen from the journals of the present year, a great deal of work on these lines was being done in the U.S.A. The U.S. Bureau of Mines were continuing their programme, and the A.P.I. were initiating one in connection with the Research Project being conducted by Lacey. Amongst fields on which bottom-hole sampling is being reported might be mentioned Oklahoma City, Crescent, Hobbs, Keokuk Falls and Sugarland.

So far, only preliminary results had been reported, and the final results would be interesting. The reason why bottom-hole sampling was now attracting more attention was that it was being more generally appreciated that, in conjunction with bottom-hole pressure measurement, there was wide scope for practical application of the data obtainable from samples of reservoir crude collected under fall reservoir pressure. In particular might be mentioned gas conservation and flow calculations in wells.

The preliminary work that had been reported so far was in one respect disappointing, although it might not prove to be so when the final results came along. It was nearly always a question of "spot" data being reported from individual wells. He had not seen, at any rate in the fields he had mentioned, nor even in East Texas, where the United States Bureau of Mines carried out their main investigation, any actual surveys of the variations in bottom-hole sample data, particularly in the "saturation pressure" of the reservoir crude in different sections of the field.

Investigations in Iran had shown that these variations might be very considerable, and also that they might be of considerable significance. There appeared to be a relation between these variations and the productivity of the reservoir, and it would be very interesting to see if similar relations were confirmed in fields of other type. If anybody was carrying out any work of this kind, he would suggest that before arriving at any conclusions from it the worker should wait until he had the data from various points in the reservoir. "Spot" data might be deceptive. There was no need to repeat all the data that had been observed on the reservoir samples. They were all related to the saturation pressure, and this was the one factor to observe at different points. The relation between saturation pressure and other properties of the reservoir crude should be determined at the highest pressures available.

It might be of some interest, in view of the fact that this subject was of topical interest at the moment, to compare the main features and advantages of the different types of bottom-hole sample taker. Although individual articles had come out, he did not think that any comparative reviews had been published. The three main types were, firstly, the flow through type, in which the crude or liquid flowed through the simple chamber whilst it was being lowered into the well and both valves were closed simultaneously at the point at which the sample was taken. The second type was the slow displacement type, in which the valves were closed until the sample was taken, and the sample was then admitted slowly, the rate of admission being controlled either by the displacement of a piston or by the displacement of a liquid. The third type was the sudden admission type, in which the sample chamber was evacuated before lowering and the sample was admitted suddenly on failure at the desired depth of a disc which protected the inlet valve The failure of the disc might be caused by some suitable timing device or by pressure.

The main advantages and disadvantages of these different types of sample taker were that the flow through type was liable to contamination from upper levels unless very careful and somewhat tiresome precautions were taken. The valves had to be comparatively large in order to allow flow through the chamber, and it was rather difficult to get a tight shut off.

Among its advantages were that it could be made fairly light and of small diameter. The slow displacement types had the advantage that there was no sudden reduction in pressure, and no gas was therefore prematurely released from solution as the sample entered the sample taker. Also the valves were small. They had the disadvantage of being too heavy to run on a piano wire. The piston controlled type had the further disadvantage of possible leak past the piston, which was difficult to shut off owing to the large joint necessary at the upper face of the piston. The slow displacement type, in which the rate of entry was controlled by the displacement of a fluid, was essentially useful for the making of pressure volume curves. Its chief disadvantage was that only very small samples could be taken, because if the size of the sample were increased it was necessary to lower the taker below the point at which the sample began to be admitted, in order to compress the gas which was holding a back pressure against the fluid being displaced.

The third type—the sudden admission type—was in many ways the most practical. Its only disadvantage was that the pressure on the sample was reduced as it entered the sample taker and gas was prematurely released from solution, but this could be overcome, after withdrawal of the sample to the surface, by pumping in mercury or water and redissolving the gas. After this, the sample could be treated in exactly the same way as a sample from which no gas had been prematurely released. Its advantages were that the valves could be very small, it was simple, there was not much chance of its leaking, it was very light, and it could be made of very small diameter. It was therefore suitable for use in tubing.

These brief remarks were necessarily incomplete, but the speaker hoped that they might be of some assistance in deciding upon the type of sample taken to be selected for any given field or purpose.

He inquired, in conclusion, whether any member present had any experience of cameras for use in wells. The purpose for which he would be interested in such a camera would be to try to get data regarding the spacing and size of fissures in the reservoir rock.

Mr. C. J. Johnson remarked that one big omission in the words of previous speakers had been that no one had mentioned the separation of oil and gas in any form. There had been an advance not so much in the knowledge of gas and oil separation, but as to the practical development of separation plant during the last year, particularly in Iran. In one of the fields with a very high pressure, a six-stage separation had again been used, the first stage being at the well-head, and the remaining five being at the storage tank, or final balance tank. Again, the well-head pressure had been utilized to carry the fluid to such an elevation as enabled it to be delivered by gravity to a pumping station sixty miles away. Thus the actual well pressure is economically employed to avoid the cost of a pipeline pumping installation. A further development was made in a field of considerably lower pressure. Well-head separators had been installed and would be operated at such a pressure as to enable the off-take gas being delivered to a plant at a pressure of 35 lb. per sq. in. In the plant, the gas is either processed at 35 lb. per sq. in., or, at this pressure, used as the first stage in compressing gas to 150 lb. per sq. in.

Mr. M. W. Strong proposed to deal with one or two small points that had not been mentioned. On the subject of drilling fluids, the question had again cropped up about obtaining suitable evidence from the reservoirs, and the conditions in them, partly from samples, and partly from coring. He and his friends had recently had experience in drilling with a 2.13 water-barytes based mud, with no salt in solution—a really thick mud. They had obtained almost uncontaminated samples from each zone, clearly defined at each foot or two, and had obtained extremely precise information as to the variation of the rocks penetrated. The only extra advantage of coring in such a well was to obtain special data pertaining to fissures and the permeability of the reservoir rock. By using a really thick mud and not allowing the samples to settle, it was possible to obtain extraordinarily exact information by ordinary rotary muds. The method had been rather overlooked. At the World Petroleum Congress questions had been asked whether it was possible to get information on muds in that way. The strictly economical side of mud was obviously the next subject in mud studies. A mud made of bentonite, a mud made of silica, and a mud made of calcite and an ordinary marl mud, if all treated with the usual chemicals available for drilling mud, gave entirely different results. As far as he knew, no detailed study of the behaviour of these muds under the different chemical treatments was yet available.

This science had a very close application to the treatment of certain heaving shales, where chemical control might be exercised on the side of the hole, and any further interference with the side by the drilling fluid might be stopped once it had been drilled.

A second point he wished to mention was the technique of use in certain types of oil-fields where difficulties arose owing to the lack of palæontological evidence in the overburden. Certain limestone fields, for instance, had an overburden of anhydrites, salt and marls which may have suffered disturbance and deformation so that drilling was blind and there was a lack of key beds indicating the approach of high-pressure formations. During 1931, in Iran, an exhaustive examination had been made of anhydrite textures and of the silica and carbonate types preserved in the anhydrites. This micropetrographic study, in which over 150,000 specimens were sliced and examined, showed that this type of work could give an extremely useful stratigraphic means of correlation, so that the drillers were no longer in the hazardous position of having to wait until they got to limestone before they knew where they were.

In well temperature work, he observed, some research had been done which suggested that there was a great deal more convection in oil-fields than was usually believed, especially in very productive parts of oil-fields, where the effect might be aided by the shape at the cap rock cover. Such effects would influence the flow of oil and the production possibilities from that area, and should be taken into consideration in assessing the data available showing the parts of the field which had free connection, and so on. The data should be correlated as far as possible with other bottom-hole data, such as pressures, levels, etc.

Mr. A. C. Hartley said there was one omission from the articles this year, about which there might be information given with advantage next year—

namely, although the development of the oil-engine, the compression-ignition engine or diesel engine had been dealt with in one or two of the articles, there was no reference to the adaptation of this very efficient and convenient form of power to driving drilling rigs. A good deal of work had been done. Electrical and hydraulic drives had been brought into play to bring the diesel engine characteristics more into line with the steam-engine. Remarks by any member on actual experience with such means for driving rigs would be extremely interesting.

Mr. A. Beeby Thompson said the first use of cameras in wells had been made, he thought, in Russia in about 1901. The Russians had designed at that time very excellent cameras for wells, mainly for photographing fissures in wells. A stereoscopic camera was put down in a chamber, compressed air forcing the liquid out of the chamber in which it was. A clear photograph was then taken of the object in the well. At that time the depth of wells had probably only been about 1200–1500 ft., so that very high pressures had not had to be contended with. Personally he thought it would be quite possible to design some sort of apparatus of the same kind to take photographs laterally of fissures. It would be quite easy to flush out the well with clear water without the necessity of pushing the liquid away with compressed air. At the time he was mentioning there had been a chamber of compressed air which had been released by clockwork, and which pushed all the liquid away so that a clear view had been obtained.

Captain W. H. Cadman mentioned one matter which he thought might be of interest to members who were familiar with the use of drilling mud. There was no novelty in the use of drilling mud in the oil industry, but overseas members might be rather amused to know that there was a novelty in the use of drilling mud in the coal industry. The oil industry had come to the help of the coal industry in the latest coal-cleaning plant, which was now protected by a number of patents and was operating commercially. This process was actually making use of ordinary drilling mud (of a specific gravity which varied according to the nature of the coal to be cleaned) for cleaning coal by the flotation principle.

The Chairman said that in the absence of Mr. Seamark, Mr. Southwell might reply to one or two questions, notably the point made by Mr. Evans in regard to the least amount of calcareous matter which would enable acid treatment to be successful.

Mr. C. A. P. Southwell replied that he was afraid that he could not give any precise data on that point. Actually the instances in which acid treatment had been used in Iran were those limestone formations which had naturally a high content. Personally he could not answer in so far as it would affect a sandfield, for example, or some field where the calcareous matter was probably very low. He did not know whether it had been tried out in the sandfield of very low calcareous content. He could only reply, therefore, that laboratory research would indicate whether there was a possibility of success and this should be undertaken.

Mr. M. W. Strong said he was not aware that his Company had measured the lime content of marls in connection with fishing by acid treatment. Where the content of calcium carbonate had been measured in marls they averaged 30 per cent. by weight, but sometimes approached 60 per cent. The minimum proportion of carbonate necessary to justify the use of acid in freeing tools depended so largely on the type and texture of the rock that he could give Mr. Evans no minimum figure.

The Chairman said that Mr. Evans might be able to throw a little light on the subject of photography in wells and might also be good enough to reply to one or two queries which had been addressed to him by Mr. Strong on the subject of drilling muds.

Mr. P. Evans, in response to the Chairman's query, remarked that the point about the camera struck him as being a very simple one up to the stage of getting outside the container. He did not think there would be any difficulty in designing a camera and container which would go down to any ordinary depth, say 5000 or 6000 ft., and which would take stereoscopic photographs, as Mr. Beeby Thompson had suggested; but he thought it might be a little difficult to get a reasonably clear solution outside. The actual construction of the camera itself, and an arrangement for taking photographs at any particular depth, should not present any special difficulty, but whether a photograph would be clear or whether it would be very much blurred by the amount of material suspended in the water, or by deposits of mud or oily material on the plate-glass which would necessarily form part of the shell, seemed somewhat doubtful. He did remember some years ago seeing a reference in one of the papers to a camera that had been put down a well, but he had no idea as to the construction of it, or what had been done.

With regard to the Chairman's reference to mud and chemical treatment, he felt that it was scarcely possible to touch on the subject without unduly prolonging the discussion. The only point he would like to make was that in the work which they had been doing in Burma and in Assam they had realized the extraordinary complexity of the problem. It was often found very difficult to get two muds, apparently almost similar, to behave in precisely the same way, and he felt that many years of work by a large number of chemists were ahead before they could say that they had got the chemical side of the study of mud on to a satisfactory basis. One of the things which they had thought necessary first of all had been to try to straighten out in some small way the physical side. Until it was possible to take measurements of physical properties which could be repeated—measurements which really did mean something—and until a measurement which was made in Burma could be compared with a measurement made in Assam or Iraq or the United States—he did not think there would be very much progress in co-operation between investigators in different fields. Consequently, during the past few years, the mud work which they had been doing in Burma and Assam (apart from the ordinary straightforward routine work which they had to do from day to day as conditions had called for it) had been directed mainly towards trying to establish some means of comparison of quite different types of mud as regards

physical properties, such as viscosity and thixotrophy, and physico-chemical properties such as hydrogen-ion concentration (*i.e.* acidity, alkalinity), and salinity. They felt they had first of all to clear the ground and get some reasonable and generally applicable standards of comparison before different workers could utilize to the fullest extent the very great amount of work which, in different parts of the world, was being put into problems which had a direct or indirect bearing on the chemical aspects of drilling fluids.

The Chairman said that all would agree that they had had a very interesting and useful discussion, and he would point out that subsequent written contributions would be welcomed. In conclusion, he thanked the authors for their reports, the speakers for their contributions to the discussion and everybody present for their attendance.

Mr. B. J. Ellis, in a written contribution, said that the compilers of the reports on drilling, production and transportation had been so concise that the casual reader might assume, from a comparison of the amount of matter written on those subjects and on refining, distribution and use, that there had been little progress on the field side.

Actually there was very definite progress in drilling; wells were completed to greater depths, drilling speeds were increased and drilling costs were lowered. The old bugbear of crooked holes was finally conquered, and the art of controlling deviation was so mastered that intentional deviation of wells in a given direction became possible, and was used for the development of otherwise inaccessible oil sources and for the bringing under control, by water flooding, of producing wells that had blown-out and cratered.

The improvement in drilling may be almost entirely attributed to the better understanding and use of drilling muds, and the industry is definitely indebted to those who have carried on the necessary research work, often in addition to their ordinary duties and without the facilities for research which our opposite numbers enjoy.

There has been very little trouble with drilling equipment with the exception of mud pumps, hoses and swivels, the designs of which need revising to meet the high mud pressures and tremendous loads of drill-pipe now being carried. This work is at present in hand, and this year should see these difficulties solved.

Drilling bits have been improved, particularly those of the roller type, both for the drilling of hard and soft formation, and they are now able to stand up to much higher rotational speeds. There has been practically no improvement in core barrels, and, although one or two new types have been produced, the perfect coring tool has still to be developed.

Drill-pipe, with the new full-hole tool joints, stood up remarkably well to the increased depths of drilling, and there does not appear to be any necessity meantime for a revision of the A.P.I. standards except possibly in the direction of higher tensile steels and more thorough heat treatment.

On the production side, research added considerably to the knowledge of the physical properties of oils and gases and of the flow of liquids and gases through porous media, but it is doubtful whether any progress was actually made in bringing to the surface a greater proportion of the original

oil content of reservoirs under production. Numerous estimates have been made in the past of the percentage of the original oil content left underground at economic exhaustion, and if, at the beginning of 1934, a figure of 25 per cent. was accepted, it could not be said with any assurance that it had now been reduced to 20 per cent. or any such lower figure. This, after all, is the goal at which production research and experiment must aim, and it seems possible that there is a tendency towards too much theory and insufficient experiment in full scale. The Bradford Field is the only example of a serious attempt to tackle this question, although there were vague reports during the year of attempts in Russia to fire the oil-saturated sands in certain wells and utilize the energy of the expanding gases for driving the oil to producing wells. The circulation of superheated water, as carried out in the recovery of sulphur, has not so far been tried, and generally there has been a surprising lack of effort at greater recovery on practical lines. Oil mining is an expensive and dangerous method, and it is to be hoped that development of other ways will make it unnecessary.

Mr. E. A. Satchell writes as follows:—Mr. Southwell's figures on doubling the production of a well in Iran from 400 barrels with a 300-lb. bottom-hole differential to 800 barrels with only 5 lb. differential are most interesting and useful.

Mr. Southwell is certainly right in thinking that commercial hydrochloric acid of 30 per cent. is too strong for injecting undiluted into a well. This percentage was meant to be the convenient strength for shipping to the well where, of course, it must be diluted to suit the type of limestone. His figure of 15 per cent. tallies with the average percentage quoted by American authorities.

In reply to his query regarding sealing of the pores, it must be explained that this refers to *lime impregnated sand* in Ohio under low pressure and is given as an example of a failure (A.P.I. Bulletin 213, page 78, discussion), not a successful process for stopping up pores. In this connection Messrs. Putnam and Fry (*Ind. Eng. Chem.*, **1934**, **26**, 923) say, "In certain types of formation where this is the case (*i.e.* where the rock pressure is low), the regular acid can be forced back into the pores of the rock, but the products of reaction do not come out. The difficulty is that the acid acting on the limestone forms carbon dioxide and calcium chloride solution which exist side by side in the pores. The pressure required to force such an interspacing of gas and liquid from the pores is considerable and is dependent on four factors: (1) size of pores, (2) surface tension of the neutralized acid, (3) force of attraction between the neutralized acid and the walls of the pores, and (4) number of gas–liquid groups."

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

JUBILEE BANQUET.

THE Jubilee Banquet of the Institution of Petroleum Technologists was held at the Park Lane Hotel, London, on Friday, June 21st, 1935, the President, **Sir John Cadman, G.C.M.G.**, occupying the Chair.

"THE KING."

The Toast of "The King," proposed by **The President,** was loyally pledged.

"THE INSTITUTION OF PETROLEUM TECHNOLOGISTS."

The Hon. R. G. Menzies, K.C.: I wonder if an outsider in the oil world could tell you just how he thinks about the oil world. It is a curious thing how largely oil has, so to speak, impressed itself on the modern world, how much it has come to be discussed, how many people who are not expert at all have come to regard themselves as experts. The subject lends itself in Parliament, if I may say so, to a great deal of rhetoric. I am in Parliament myself, and I want to make that clear when I express such criticism. But in Parliament we look on the oil industry from two points of view. First of all, we abuse people very violently when they do not find oil. In Australia we have not yet found oil except in very small and reluctant quantities, although Sir John Cadman has, I believe, been in some way remotely connected with the process of extracting small quantities of oil from shale. But, broadly speaking, we have not found it yet, and the result is that in Parliament we are abusing everybody connected with oil, saying that if they were competent people they would have found oil long ago and, of course, if they had found it, it would not have been necessary to buy from other countries. On the other hand, if somebody does discover oil in Australia, we shall proceed to attack him violently for the amount of profit he is making. So there is no hope from Parliament.

Then I have heard other people attribute to oil and to the search for oil and the fight for oil most of the modern wars. Every kind of disaster has been laid at the door of the oil industry. But the truth of the thing is that when the oil era began, a new age of human development also began. It is very difficult to imagine what the face of the earth would be like to-day if it were not for this great industry, because it can be said with a very large measure of truth that most of the wonders of the last twenty years have been made possible by the discovery, the understanding, and the use of petroleum and its products. Accordingly, it is essential that this industry, with its vast power for human good or ill, should be put upon the best possible basis.

If I may say so, Mr. Chairman, there is a great disposition all over the

world, in connection with any great department of life like this, to resort easily to purely empirical methods. It is not always spectacular to master the scientific basis of a great subject. People who are devoting themselves to technical work are very seldom rewarded either by kicks or by ha'pence. But if this industry is to serve its real purpose, then every possible step must be taken to see that the people who are engaged in looking after its scientific side should be as well trained as possible and brought up to the highest standard possible.

Now, Mr. Chairman, Ladies and Gentlemen, I am sure you will all agree with me when I say that the easiest thing in the world is to aim at a low standard. Low standards are always rather popular, because it is so easy to come up to them, and, as a result, they give most of us a rather more comfortable feeling than we would otherwise have. But this Institution exists because it realizes that nothing but the highest standard should be aimed at when discussing the scientific aspects of a great modern industry of this kind. I can say for myself, as one connected entirely with other branches of professional work, that I wish this Institution every possible success. I wish it well in the war on the quackery that still exists in some so-called oil circles in the world, and I hope, as a result of its first twenty-one years of life and the years it has in front of it, it will make a notable contribution to the solving of those problems with which so much of human progress is bound up. (*Applause.*)

The President : It is a source of much gratification to me that the Attorney-General, Mr. R. G. Menzies, of that great Dominion, Australia, should have attended our dinner to-night and proposed the Toast of The Institution with such eloquence. We all welcome him and his charming lady. I could say much more about Mr. Menzies, who I venture to think will in the future be heard much of in Empire affairs; but I must not trespass on the province of the next speaker.

As we have been reminded, the I.P.T. is now twenty-one years of age. Before its birth there was no centre where the various technologists concerned with petroleum could meet for an interchange of ideas, nor was there any medium for the dissemination of fresh knowledge or for the stimulation of thought on the many problems of oil.

In 1914, therefore, some of us, including the late Sir Boverton Redwood, decided to form the Institution.

To-day, we have 1343 members dispersed throughout the world; and we can justly claim, I think, that the Institution has more than fulfilled the hopes of its founders.

The Institution has from the outset issued a scientific journal in which, as well as recording its own proceedings, it has published and discussed reports of researches, scientific and technical papers and contemporary petroleum literature.

The Institution has aided research to the fullest extent permitted by its financial resources, and has subsidized a series of important investigations. Branches, each of which is an epitome of the parent body, have been established throughout the world. By means of them members in very many countries are able to meet and discuss and exchange ideas and experiences.

In an industry such as that of petroleum it is essential to establish methods of testing that are acceptable to all parties, whether producers or consumers. From the Institution's earliest years it has developed a standardization of petroleum testing, and its well-known manual on this subject is in the third edition.

In the sphere of international affairs, the Institution successfully organized the first World Petroleum Congress, which in 1933 brought to London many hundreds of petroleum technologists from all parts of the world. The success of the first Congress naturally leads to the expectation that further gatherings of the same nature will be held in various centres.

All these activities are a drain upon financial resources, and the work that can be done depends always on the amount of money available. With more money, many more publications could be issued, and with less delay; methods of testing could be more frequently revised; valuable statistical data could be collected; branches could receive greater help. In general, existing activities could be improved and new activities could be undertaken.

During its life of twenty-one years, the Institution has accumulated a small capital, which, however, is very inadequate. It is hoped before long to establish an endowment fund which would free the Institution from financial care and permit an enlargement of scope. There is no doubt that such a fund is needed and could be used to great advantage.

To many laymen, technical and learned societies have an element of the mysterious which appears to ally them with those secret societies which are more popular in some other countries than ours. Indeed, some outsiders have the impression that a technical society is the technologists' substitute for a religion. He notices, for example, that each society has a code of rules for its own conduct; it also imposes observances upon its members and prescribes the manner in which they shall conduct themselves, both within the society and towards the uninitiated.

Reference to a code of rules, by the way, reminds me of another code to which more adherence might be paid. I mean the endeavours now being made, under the guidance of the Minister of Transport, to regulate traffic on our roads and to diminish the annual toll of accidents. In my opinion, Mr. Hore-Belisha is doing work with a fine objective in view. In some respects, perhaps, his measures are not yet perfect; but with co-operation among all classes of road users—with helpful criticism instead of destructive—some workable scheme will ultimately be evolved.

This, however, is a digression, and I must return to my topic.

Much of the lay impression of technical societies, of course, is utterly wrong; but I do not find it distasteful to think that the scientist places his vocation—and its exercise—upon a high plane. There is something better than mere commercialism in the manner in which members of such societies as ours spread the knowledge which they have acquired. Each individual contributes something to the common fund, and, gradually, a corporate store of knowledge is accumulated to which all have added and from which all can draw. Moreover, the association which takes place within the society establishes a spirit of comradeship. To-day, for instance, a member of the Institution who visits any one of fifty-two countries will

find there some individual who is also a member and with whom there is a certainty of some interests in common.

We are proud of our society and of those who are and have been its members. We look forward also to a future in which petroleum and the Institution of Petroleum Technologists will be of increasing value respectively to the world at large and to the industry which produces petroleum and handles it in every phase from discovery to consumption.

The present occasion, when we are commemorating our twenty-first anniversary, is also the twenty-first year during which Mr. Arthur W. Eastlake has been Honorary Secretary of the Institution. We feel certain that members of the Institution all over the world will wish to express their appreciation of Mr. Eastlake's work in some appropriate and tangible manner; and a fund has been opened, and will remain open until 31st December, 1935, to which we invite all members to subscribe. The fund will be devoted to some suitable form of presentation to Mr. Eastlake.

For twenty-one years Mr. Eastlake has given devoted and unremitting service to the Institution. Without him, our accomplishments would have been less, our progress retarded, and our proceedings less agreeable. He deserves the gratitude of all members. I ask them to express it in the way I have just suggested; and I ask all present now to let Mr. Eastlake hear that applause which is a reward he has well earned.

"The Guests."

Dr. A. E. Dunstan (Past-President): Before I begin my few remarks I am asked to read this telegram from a senior Past-President, Sir Thomas Holland, "Wishing you a most successful dinner and long life to the Institution."

To-night, as the President has indicated, we have a very special event and a very particular occasion to celebrate. First, in our turn, we wish to celebrate the Silver Jubilee of His Majesty the King, under whose beneficent reign our industry and our Institution have both prospered so exceedingly. The Council have commemorated this Jubilee occasion by sanctioning the issue of a special volume which gives in a short and simple fashion a historical retrospect over this great period.

Secondly, this particular event marks our own coming of age. One can only imagine what a delight it would be to our great founder and those associated with him to see this Institution grown up to man's estate.

I now pass to our distinguished and honoured guests, and it would be a work of supererogation to refer to all of them. Mr. Menzies requires no introduction from me. You have heard, and appreciated and approved, that remarkable forensic style which is characteristic of him and his great profession. We welcome him, as the Chairman has said, *con amore* because he represents that great other half of us in the Southern Hemisphere.

We welcome also the Secretary for Mines, Captain Crookshank. Indeed, we regard him as one of ourselves. We remember with immense gratitude the extremely good work his predecessor did for us on the occasion of our World Petroleum Congress, and we look forward to the new Minister as being at least as good a friend, and to constant collaboration with him in the multifarious problems arising out of fuel.

I pass to Sir Frank Smith, Secretary of the Department of Scientific and Industrial Research, Secretary of the British Association and Secretary of the Royal Society. In Sir Frank Smith we have a representative of all that is best in the scientific life of the country. We in the Institution have good cause to appreciate the excellent work done by his Department in the application of scientific methods to industrial problems, and we wish to associate ourselves with the great efforts of his Department in everything that pertains to fuel technology, and to congratulate him and his Department on the work done by the Fuel Research Board, particularly in connection with the many problems of the fluidification of coal. We wish to give particular appreciation to that effort of his Department in bringing scientific methods into industrial problems. It is obvious that the D.S.I.R. leads the way in the application of scientific activities to industry.

I come to Sir Charles Bressey, the Chief Technical Adviser on Road Transport in the Ministry of Transport. Our own work is intimately connected with the road, and it is therefore very appropriate that we should welcome Sir Charles on this occasion. Road transport, one may fairly think, has been somewhat harassed in its effort to attain perfection. We ourselves are particularly concerned with the fuelling of the road vehicle, our engineering brothers with the development of the high efficiency engine. Between us we strive for the ultimate best, and all we can give in the direction of scientific and technical help will be freely available.

From the road we pass to the air. We welcome Air-Marshal Sir Hugh Dowding, of the Supply and Research Department of the Air Ministry. More and more are we concerned with aviation in this Institution. We shudder to contemplate what new demands may be made on us for higher and higher knock-rating values. We have seen in our retrospect anti-knock values rising steadily, and the fuel technologist painfully plodding and trying to keep up with the demands; but not yet have we failed to provide the appropriate fuel.

Mr. Starling, of the Petroleum Department, Ministry of Mines, is a particularly good friend of ours. When the first World Petroleum Congress was being hatched, Mr. Starling took a great part in the incubation, and the chick turned out not too badly. We are grateful to him, and we look forward with expectation for further favours to come.

I have the particular honour to associate this Toast with the name of Sir William Bragg, Director of the Royal Institution, Fullerian Professor of Chemistry, and joint Nobel prizeman with his son. Sir William Bragg is a great figure in our science. His work is characterized by the penetration of his own X-rays and the clarity of his own crystal structures. He is a great leader, a great pioneer, and a great discoverer. (*Applause.*)

Sir William Bragg, O.M., K.B.E., F.R.S.: My first duty, of course, is, on behalf of your fortunate and happy guests, to say "thank you" most cordially for your very kind entertainment to-night. We want to congratulate your Society on the success that has attended its activities. It is a fine society, doing fine work, and I am sure that the measure of its usefulness is beyond anything yet realized. And you have got a very fine President this year in the person of Sir John Cadman.

I must return thanks for those whom Dr. Dunstan has named, and I

would especially refer to Mr. Menzies. I am proud of Australia, having lived there for many years; and it is always a pleasure to me to see Australians honoured. Australia, whether or no she ever strikes oil in the liquid form, strikes it in the form of great personalities among her sons.

Your Society is one of a group that have been formed within the last fifty years or so. One thinks of the Institutions of Civil Engineers, of Mechanical Engineers, of Electrical Engineers, and of others. Each of these links together the men engaged in an industrial enterprise, and does so both for their own good and for the good of the community. You must go back nearly two hundred years before you find a similar outbreak of society making, to a time when there were formed in almost rapid succession certain great societies of a nature and purpose differing from yours. And yet they may be regarded as your ancestors. Italy was the first, with its Academy at Florence founded *c.* 1657; then came the Royal Society in England in 1662, then the French Academy in 1666 and then at the end of the century the Academy in Berlin. Not that people had not assembled together before in order to discuss scientific matters of interest to them, but those were the dates when the societies took official form.

There is a great deal of interest in comparing those old societies with the group which has been formed during the last half-century, because it marks the extraordinary change that has come over the relation between science and industry. When the Royal Society was formed in the middle of the seventeenth century, industry was a matter of individual craftsmanship, and the first members of that Society and of like societies on the Continent were not men who were assembled because they belonged to a particular business, but, as some of them were very careful to explain, because they had none at all. Spratt, an early historian of the Royal Society, wrote appreciatively of the fact that they were gentlemen of leisure, with ample means, and often of noble blood—a comment scarcely applicable to our Societies of to-day. But these men laid it upon themselves to gather up every variety of observation and information from all parts of the world, and to discuss them with one another and write about them in their "Transactions." In fact, it was a favourite device of theirs to send out questionnaires, to different countries—to India, to America, and elsewhere—and ask all sorts of strange questions about what they had heard went on in those countries, and whether it was true. You would be amused at some of their queries, but I must not protract my speech by telling you of them.

In those days the members of these societies did actually concern themselves with the industrial affairs of their country, being interested in the problems with which industry was faced. One of them was the ventilation of mines. The very first paper ever recorded in the Royal Society's "Proceedings" is a paper on the ventilation of mines in Belgium. Again, they devoted much time to the question of the tides. It was becoming highly important to calculate as closely as possible the times of high and low water because a trade with America was now springing up. Ships to cross the ocean must be bigger than had been the custom, and these could not get into the little harbours of England except at certain times which must be known.

In such way there was an attempt on the part of these older Societies to solve problems that were of interest to the nation. But this is the point I would like to make, that science waited entirely upon industry. It had nothing to suggest to industry at that moment. All the craftsmanship was handed down from one generation to another in local circles from father to son, from master to apprentice, and nothing was borrowed from science. The great difference of to-day lies in the reversal of the position; science has gone so fast and so far that it can propose to industry possible lines of advance. It has become important to industry to watch the advances of science. Modern industries are becoming more dependent on the scientific laboratories, and those modern industries in England which are most successful depend in many cases directly on science.

That is at bottom why your modern societies have come to be founded and to be so necessary. Scientific research is now playing a great part in industry, and you who are interested in it, or even engaged in it, feel yourselves obliged to assemble together for mutual help and consultation. It does make one realize how very important these modern societies are, and how necessary it is that the cause of science and its applications to the industrial life of the nation should be encouraged in every possible way.

We have all thoroughly enjoyed your hospitality, and we have nothing but gratitude to you in our hearts, and we wish your Institution every possible success.

THE BOUNDARY FRICTION OF OXIDISED LUBRICATING OILS.*

By E. R. Redgrove, Ph.D., B.Sc., F.C.S. (Member).

SYNOPSIS.

The static friction of medicinal paraffin containing small percentages of various fatty acids has been determined on a special apparatus, and has been found to decrease with increase of temperature. The reduction in friction produced by the fatty acids is proportional to the length of the hydrocarbon chain, normal to the bearing surfaces, attached to the adsorbed polar group.

Non-volatile acids formed by the oxidation of mineral lubricating oils eliminate the friction/temperature rise which normally occurs with unoxidised mineral lubricating oils; certain of these acids are assumed to be multipolar and to form an adsorbed film which is very resistant to mechanical rupture. Solid decomposition products cause an increase in static friction.

Introduction.

Although much study has separately been devoted both to the oxidation and oiliness of lubricating oils, it is only comparatively recently that the importance of studying these two properties in conjunction with one another has been realised. Gilson [1] showed that the friction of an unloaded bearing was greater in an atmosphere of hydrogen than in an oxidising atmosphere, and Stanton [2] found a great difference between the seizing temperatures of two mineral oils which were otherwise almost identical. Investigation of the cause of this difference by Hardy and Nottage [3] showed that it was an oxidation phenomenon, and that the lubricating value of a mineral oil could be temporarily reduced by percolating the oil through chemically clean glass beads or silica chips. Further work by Dover and Appleby,[4] by Nash, Stanley and Bowen,[5] and by Batchelor [6] showed that the friction of an oil is lowered by mild oxidation, and, finally, the researches of King [7] have shown that the lubricating value of mineral oils under oxidising conditions is governed by a suitable blending of different components.

The experiments about to be described were conducted during the period 1927–1931 and since their completion much further work has been done by other investigators, but because of the importance of the subject, due to the increasing temperatures at which lubricating oils are required to function, to the changes which are taking place in the methods of refining and in the composition of bearing alloys, it is hoped that an account of this earlier work will stimulate further research from both the scientific and practical points of view.

All lubricating oils contain organic acid to a slight extent which invariably increases under even the mildest oxidising conditions of service.

* Paper presented for discussion at the One Hundred and Sixty-fourth Meeting of the Institution of Petroleum Technologists, April 9th, 1935.

When the conditions are more severe, a great variety of oxygenated compounds is formed, including highly reactive volatile acids, less volatile acids which are relatively inert and when isolated rapidly polymerise to resinous solids, asphaltic, pitchy and even carbon-like material. The formation of such a diversity of decomposition products is due to the complexity of the molecules resulting in oxidation, reduction, cracking, polymerisation and distillation taking place at the same time and to an extent depending upon the conditions and the type of oil. It was desired to ascertain whether or not these oxygenated products were, like the higher molecular-weight fatty acids,[8] beneficial to lubrication.

Preliminary Experiments.

As a foundation for the investigation, a known mineral oil by itself and when blended with known fatty acids was tested on the Stanton Pendulum Machine.[9] This machine, although a brilliant conception, was found to possess many disadvantages as an instrument for a protracted research. Due perhaps to the high pressures employed, just over two tons per square inch, it was found impossible to prevent excessive wear of the edges of the bearing surfaces, with the result that a Michelle effect was soon created and the extremities of the tracings of the dampings fell upon curved instead of upon straight lines; reconditioning surfaces was a delicate operation for a highly skilled mechanic. In addition, a considerable amount of oil, which might not always be forthcoming, was required for each test and it was almost impossible adequately to control the temperature of the bearing. The outstanding point noticed during this series of tests was the remarkable smoothness of the swing of the pendulum when running on the 1 per cent. palmitic acid blend; there was a complete absence of "judder" when the motion reversed and the tracings were very consistent, whereas with the other blends there was considerable difficulty in obtaining duplicate readings within a 3 per cent. limit. Observation of the temperature during the progress of the tests indicated that there was undoubtedly a slight, if not appreciable, variation of the coefficient of friction with temperature, and it was decided to conduct further investigations on an apparatus where temperature could be carefully controlled, and where only a small quantity of oil—a few ml.—would be required to determine the coefficient of friction. The results obtained on the Stanton Pendulum Machine are given in Table I.

Table I.

Friction Tests—Stanton Pendulum.

Oil.	Mm. decrease for 30 Oscillations.	Coeff. of Friction, μ.
Castor	43·6	0·113
Mineral Oil "G"	53·4	0·138
" + 1% Oleic Acid	44·1	0·114
" + 1% Crotonic "	52·4	0·135
" + 1% Palmitic "	32·4	0·084
" + 1% Valeric "	52·8	0·136
" + 1% Butyric "	53·5	0·138

A simple and inexpensive apparatus was designed (Fig. 1) in which a plane slider made of case-hardened steel was supported on three ordinary steel-ball bearings, which were contained in a steel cup and held in position by a bevelled locking-ring; if the surface of any of the balls became scratched, the locking-ring was released and a fresh surface was presented by slightly rotating the damaged ball. A guard ring controlled the lateral movement of the slider, preventing it from slipping entirely off the bearing surfaces, and so becoming contaminated. This apparatus was enclosed in a lagged metal box through which a stream of purified and dried air could be passed, and an electric heater was provided. The whole was mounted on a table which by means of a worm and wheel gearing could be tilted

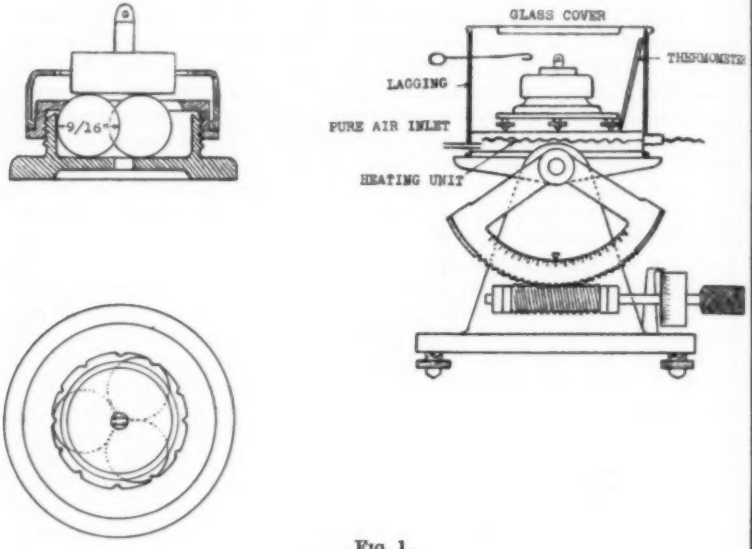


FIG. 1.
STATIC FRICTION APPARATUS.

until the angle was attained at which slip of the slider occurred. Considerable difficulty was experienced in obtaining a satisfactory surface for the slider, because continued polishing tended to produce a wavy or eggshell finish, and it was found that the best method of procedure was to lap the surface with flour of emery mixed with the oil the coefficient of friction of which it was desired to determine, subsequently washing the slider thoroughly with petroleum ether, refluxing with pure absolute alcohol, and immediately after the alcohol film had evaporated, covering the surface with the oil under test; the ball bearings were similarly washed because it was found that petroleum ether by itself was incapable of completely removing a strongly adsorbed lubricant from the bearing surfaces.

In order to test the capabilities of the apparatus, it was thought desir-

able first to ascertain the effect produced by adding to a mineral oil increasing proportions of an acid known to possess in a high degree the power of reducing the coefficient of friction of a mineral oil; the mineral oil (Oil W) chosen for this series of experiments was a highly refined medicinal paraffin oil, and mixtures were made containing 0·01, 0·05, 0·10, 0·25, 0·50, 0·75, and 1·00 per cent. of palmitic acid. On account of the low solubility of palmitic acid in the mineral oil, it was necessary to warm and vigorously to agitate the mixtures until they were homogeneous before applying them to the bearing surfaces. The same treatment was applied to all, because even the 0·10 per cent. mixture showed a faint

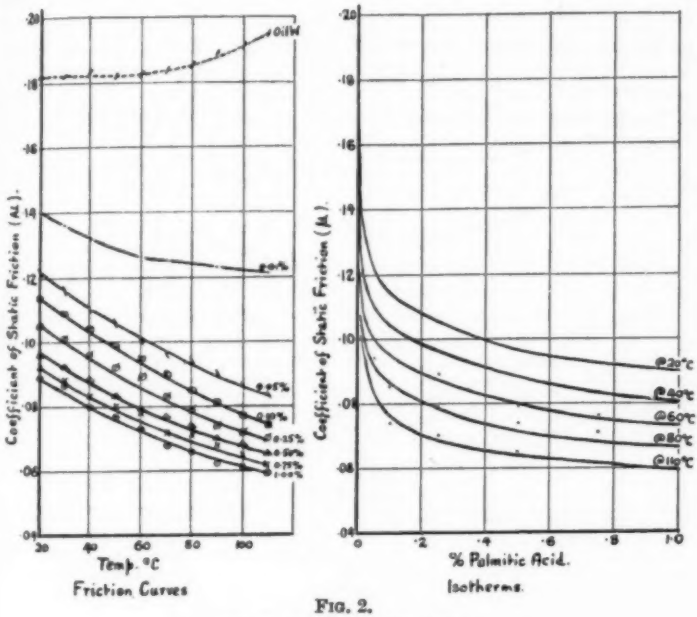


FIG. 2.

OIL W PLUS PALMITIC ACID.

cloud after standing for several days. The temperature/friction curves for Oil W and these mixtures are shown in Fig. 2, and it will at once be seen that the friction of the mineral oil at 20° C. is reduced 22 per cent. by only 0·01 per cent. of palmitic acid, and that the sharp rise in friction which occurs at temperatures above 70° C. is entirely eliminated. There was a steady fall in the coefficient of friction with increase of temperature of all the mixtures, as is clearly shown by the isotherms, and the trend of the curves indicates that when 1 per cent. of acid is present the effect is approaching, but has not attained, the maximum. When more than 0·5 per cent. of acid was present, the great oiliness of the mixture was very apparent, and it was sometimes difficult to decide exactly when slip occurred, because it was found that very slow movement (of the order of 0·001 cm. per sec.)

took place at an angle of inclination corresponding to a coefficient of friction of 0·028.*

The next step was to confirm the results indicated by the experiments conducted on the Stanton Pendulum, particularly that the lower molecular-weight fatty acids do not possess the power to effect any appreciable reduction in the coefficient of static friction of a mineral lubricating oil. In view of the sparing solubility of some of the higher molecular-weight fatty acids, it was thought desirable to use only 0·5 per cent. of acid dissolved in Oil W. The acids chosen were propionic, butyric, valeric, caprylic,

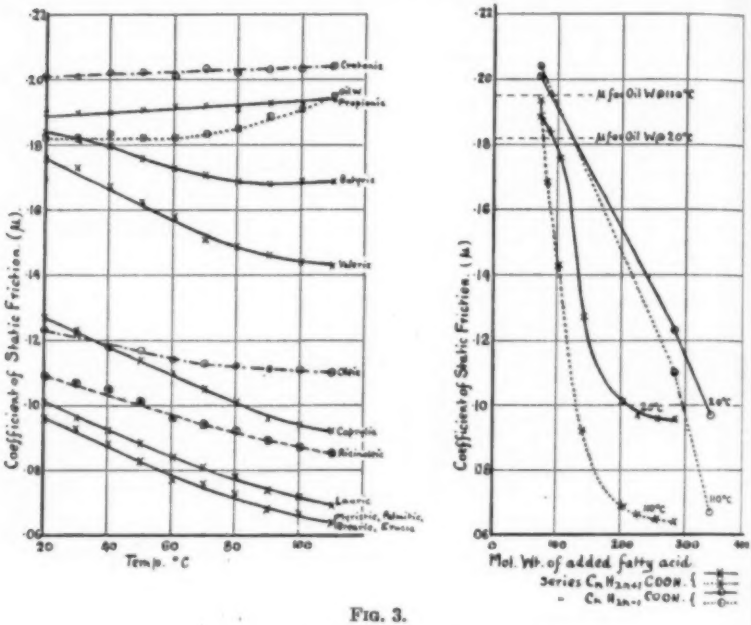


FIG. 3.

MIXTURES OF OIL W, 99·5%; ACID 0·5%.

lauric, myristic, palmitic, and stearic, representing the $C_nH_{2n+1}CO_2H$ series: crotonic, oleic, and erucic, representing the $C_nH_{2n-1}CO_2H$ series and the hydroxy acid, ricinoleic acid, $C_{17}H_{32}(OH)CO_2H$. The results obtained are given in Fig. 3. There is no doubt that the acids, crotonic and propionic, tended to increase the static friction of Oil W, and this action may be due to a tendency of the acids to combine with the bearing surfaces by direct chemical union of the primary valency type; readings were difficult to obtain, were subject to wide variation, and movement of the slider was characterised by marked harshness. With increasing molecular weight of the added fatty acids there was a noticeable reduction

* This very slow movement may have been due to earth tremors, although precautions were taken to eliminate such a possibility.

in friction, "oiliness" became more and more apparent, the very slow movement at slight inclination again occurred, and it was scarcely possible to differentiate between the results obtained with the palmitic, myristic, stearic, and erucic acid mixtures. Curiously enough, the effect produced by the oleic acid was much less than might have been expected in view of the fact that the molecular weight of the acid is greater than that of palmitic acid. From observation of the motion of the slider the impression was gained that the property of "oiliness" was not very apparent, and if the expression may be used, the lubricant seemed unsympathetic to the bearing surfaces. In Fig. 3, in addition to the friction/temperature curves, the results are analysed with the view of showing the reduction produced in the friction of the mineral oil as a function of the molecular weight of the fatty acids added, and it would appear that the effect is closely related to the length of the hydrocarbon chain attached to the adsorbed polar group of the fatty acid, for, on referring to the calculations made by Langmuir,[10] it is seen that the length of the molecule of palmitic acid is very similar to that of stearic acid, and rather more than twice the length of the oleic acid molecule.

Oxidation of the Mineral Lubricating Oils.

In order to investigate the extent to which the acids formed during the oxidation of a mineral oil influence lubricating value, various specimens of commercial oils were subjected to treatment in the Air Ministry apparatus for periods of 1 hour and upwards; four typical types, also Oil W, will be considered. Oils B, E, and G are distillate oils from Russian naphthene, asphalt, and mixed base crude, respectively, and Oil K is a blend of distillate and filtered bright stock both from Pennsylvanian, paraffin base crude, the usual commercial tests of these grades being given in Table II.

Table II.

Test.	B.	E.	G.	K.	W.
Specific gravity at 60° F. . .	0·910	0·934	0·921	0·885	0·885
Redwood I viscosity at 70° F., secs.	1272	1542	1296	1002	—
" " at 100° F., secs.	411	442	441	362	264
" " at 140° F., secs.	133	138	142	140	99
" " at 200° F., secs.	53	51·5	56	57	—
Closed flash-point, ° F. . . .	390	375	445	410	—
Cold Test, ° F.	0	0	23	28	—
Acidity, mgms. KOH per 100 gms. .	5	2	2	5	1
Coke value, % (Ramsbottom) .	0·23	0·19	0·25	0·57	0·06
Sulphur, %	0·18	0·28	1·27	0·16	—

After each period of treatment, some or all of the following points were examined:—

(1) Increase in viscosity at 100° F.
(2) Percentage of hard asphalt formed.
(3) Ramsbottom Coke Value.
(4) Amount of acidity developed.

Observation of the rate of growth of asphalt is interesting, and would appear to be an indication of the care exercised in refining, quite apart from the ultimate chemical stability of the product. Fig. 4 shows that after 6 hours' oxidation Oil K has only a trace of asphalt, whereas Oil B, the next in order of ultimate stability as judged by the 12-hour test, shows the formation of asphalt after only 1 hour's oxidation, an indication of unsuitable or incomplete refining which is also revealed by other methods. On the other hand, Oil G shows no asphalt whatever after 1 hour's oxidation; whether this unexpected behaviour is due to the presence of some substance or substances which act as inhibitors of oxidation, or whether

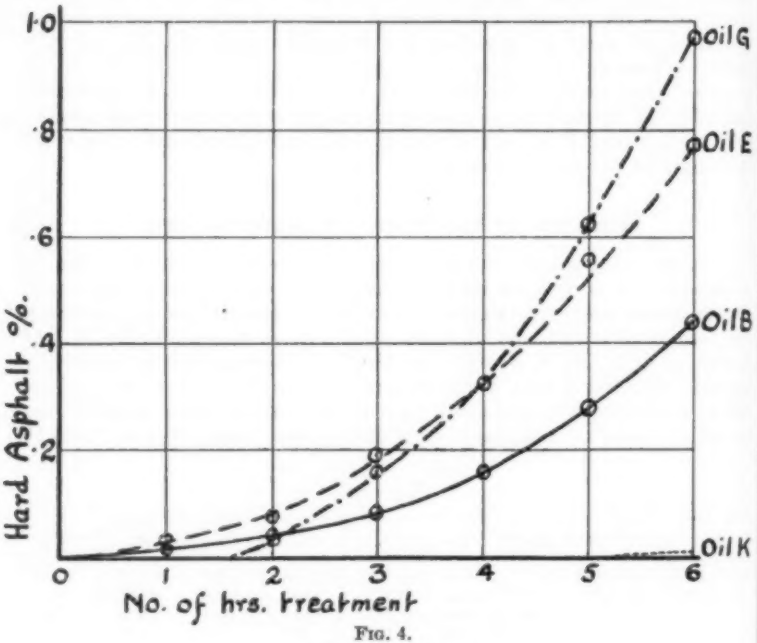


FIG. 4.

GROWTH OF ASPHALT.

skilful refining has overcome the inherent disadvantages of the crude, there is so far insufficient evidence on which to formulate a hypothesis. In contradiction to the behaviour of Oil G, cases have come under notice in which the early rate of increase in asphalt formation has not been maintained. Figs. 5, 6, 7, and 8 give the general deterioration curves of the five oils under consideration. Considering first the viscosity changes, the increase is in part due to evaporation, in part to polymerisation, and in part to asphalt formation, but there is no definite relationship between viscosity increase and any one of these three factors; so much depends on the type of crude, the degree of refining, and the nature of the constituents. Whilst the asphalt curves are useful indicators of chemical

stability in so far as most distillate oils are concerned, and there is generally a close relationship between the curves for asphalt and coke value, the similarity breaks down completely in the case of oils containing residual stock because the residual stock, or similar product of low volatility, generally oxidises to tar or pitch which may contain very little asphalt, although possessing a high coke value.

Visual examination of the various samples of oxidised oils showed that there was a considerable difference between the four types in respect of their ability to hold in solution the asphalt formed from them during their decomposition, and the oils were examined microscopically, the

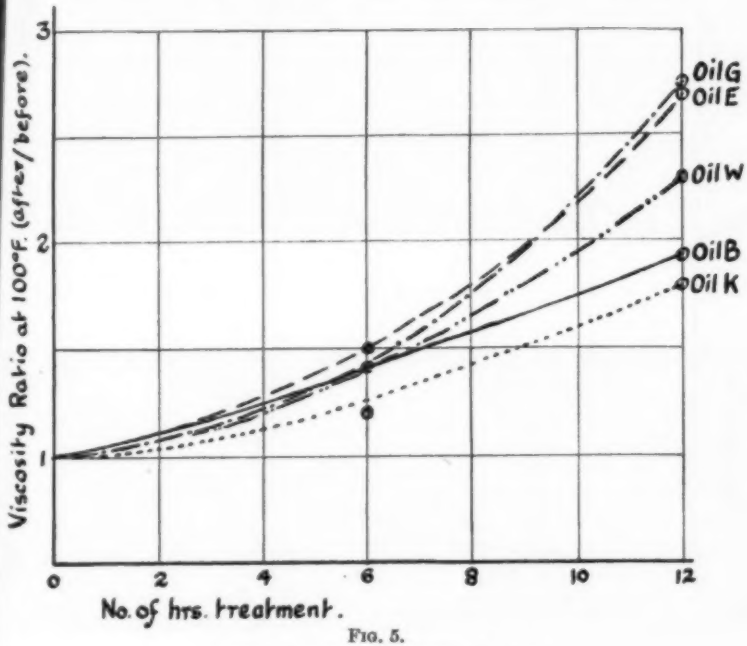


FIG. 5.

VISCOSITY CURVES OF OXIDISED OILS.

degree of magnification being about 350. On referring to Plate I, it will be seen that Oil B is showing a separation of solid material after 2 hours' treatment when the hard asphalt concentration is only 0·047 per cent. Oil E after 2 hours' treatment showed no separation of solid material, although the hard asphalt content was 0·078 per cent., and the subsequent precipitation of asphalt is depicted in Plate II. Oil G is rather remarkable in respect of its asphalt-forming characteristics. After 1 hour's oxidation no asphalt whatever is formed, and there is a visible precipitation of asphalt only when the percentage present has reached about 0·6—Plate III. The high degree of stability of Oil K results in there being no formation of asphalt after 4 hours' treatment, although the coke value

shows an appreciable increase; after 6 hours there are traces of asphalt, but even after 12 hours' oxidation there is only 0·30 per cent. of asphalt, noticeable as a visible precipitate (Plate IV). These results are interesting in showing that the microscopic method of analysis suggested by Hoblyn [11] needs to be amplified by a gravimetric estimation of the hard asphalt, and have a special significance from the practical point of view. Ruling out the desideratum that no asphalt whatever should be formed, it is at once evident that when asphalt separates out from an oil, it is likely to cause trouble not only because of precipitation between the bearing surfaces, but also because actual stoppage of the oil ducts may result. An

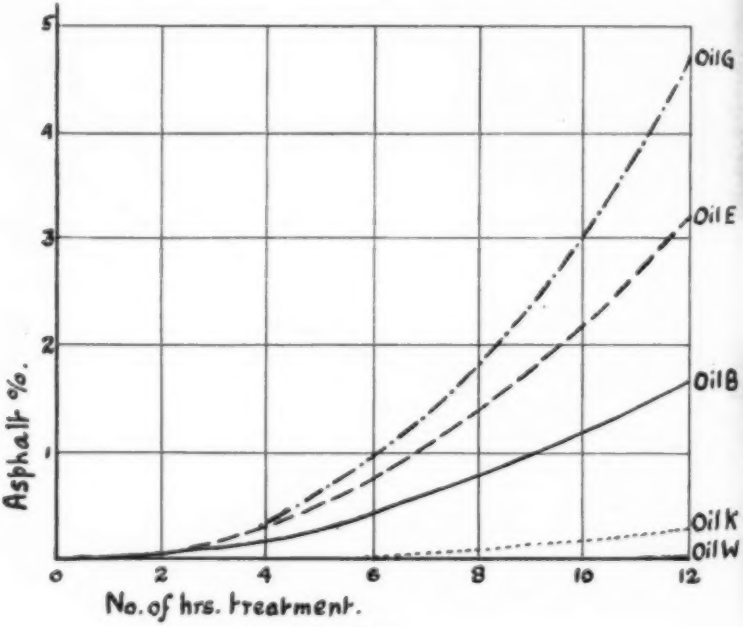


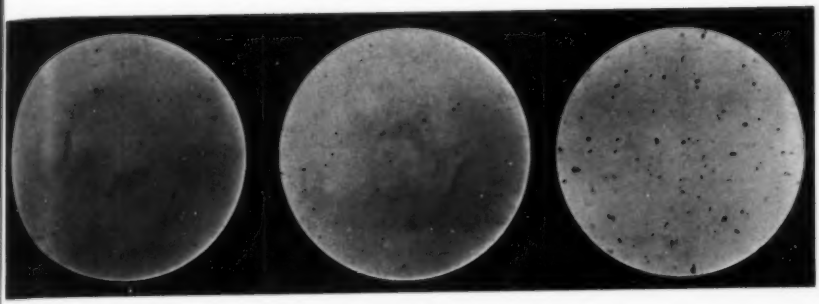
FIG. 6.

ASPHALT CURVES OF OXIDISED OILS.

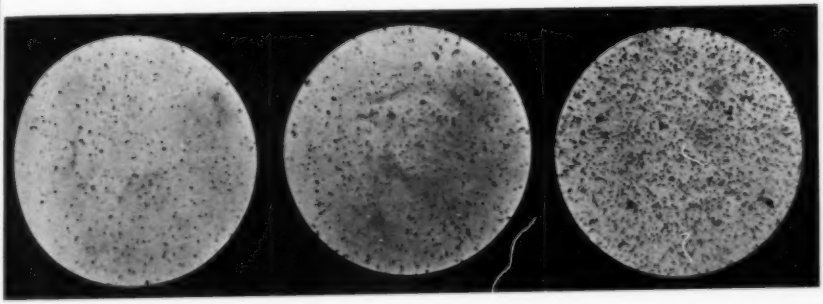
oil which throws the asphalt out of solution almost as soon as it is formed is very amenable to filtration, and, provided the filters are efficient, the oil in circulation is kept continuously clean; there is far less tendency for emulsions to form and for there to be a rapid precipitation of a large amount of asphalt previously held in solution. On the other hand, an oil which holds its asphalt in solution may to a certain point—the point of breakdown—possess the advantage if there are no filtering arrangements in the system, as there will be no precipitation on the bearing surfaces and in the oilways; the danger is from the increased liability to form emulsions and for rapid precipitation to occur. Cases have come

PLATE I.

OXIDATION OF OIL B.



(i)	(ii)	(iii)
(*a*) 2	(*a*) 3	(*a*) 4
(*b*) 0·047%	(*b*) 0·086%	(*b*) 0·16%



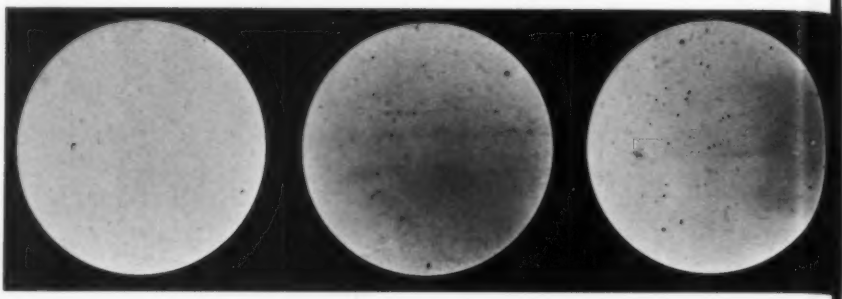
(iv)	(v)	(vi)
(*a*) 5	(*a*) 6	(*a*) 12
(*b*) 0·28%	(*b*) 0·44%	(*b*) 1·66%

(*a*) No. of hrs. oxidation.
(*b*) Hard Asphalt.

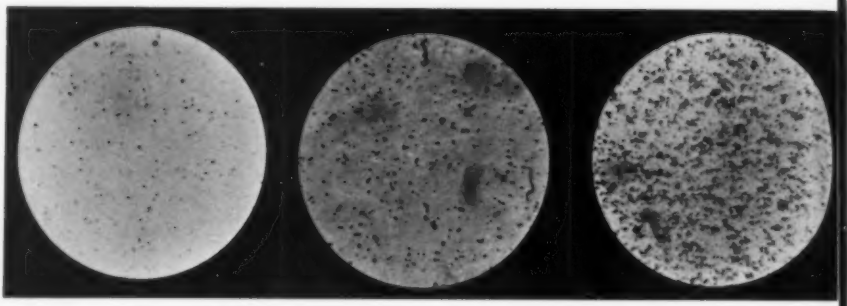
To face p. 630.

PLATE II.

OXIDATION OF OIL E.



(i)	(ii)	(iii)
(*a*) 2	(*a*) 3	(*a*) 4
(*b*) 0·078%	(*b*) 0·19%	(*b*) 0·32%

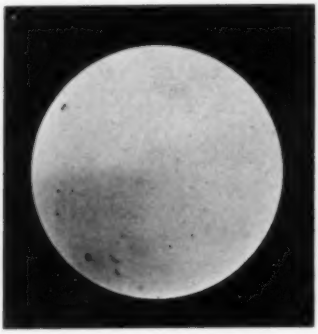


(iv)	(v)	(vi)
(*a*) 5	(*a*) 6	(*a*) 12
(*b*) 0·56%	(*b*) 0·77%	(*b*) 3·20%

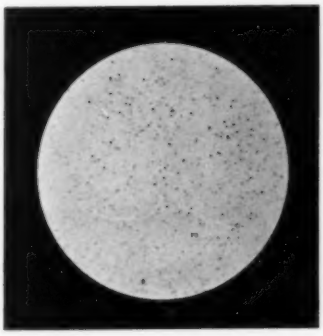
(*a*) No. of hrs. oxidation.
(*b*) Hard Asphalt.

PLATE III.

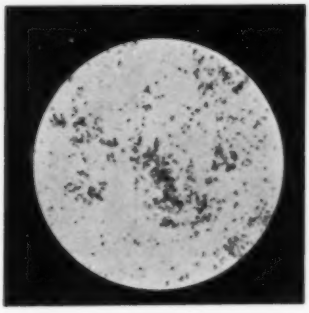
OXIDATION OF OIL G.



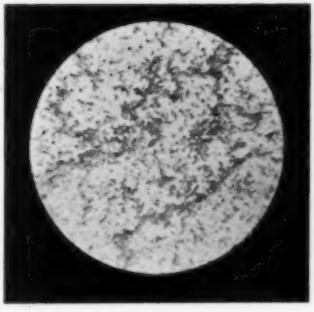
(i)
(*a*) 4
(*b*) 0·33%



(ii)
(*a*) 5
(*b*) 0·63%



(iii)
(*a*) 6
(*b*) 0·97%

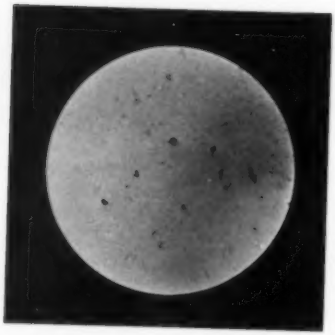


(iv)
(*a*) 12
(*b*) 4·73%

(*a*) No. of hrs. oxidation.
(*b*) Hard Asphalt.

PLATE IV.

OXIDATION OF OIL K.



12 hrs'. oxidation.
0·30% Hard Asphalt.

under notice in which the addition of fresh oil as "make up" has caused almost immediate precipitation of the whole of the asphalt previously held in solution.

Although it is thought that the petroleum acids formed during the oxidation of an oil are the progenitors of asphalt, they do not seem to be related in any definite way to the amount formed, a fact which is very apparent when the readings obtained on Oil W are considered.

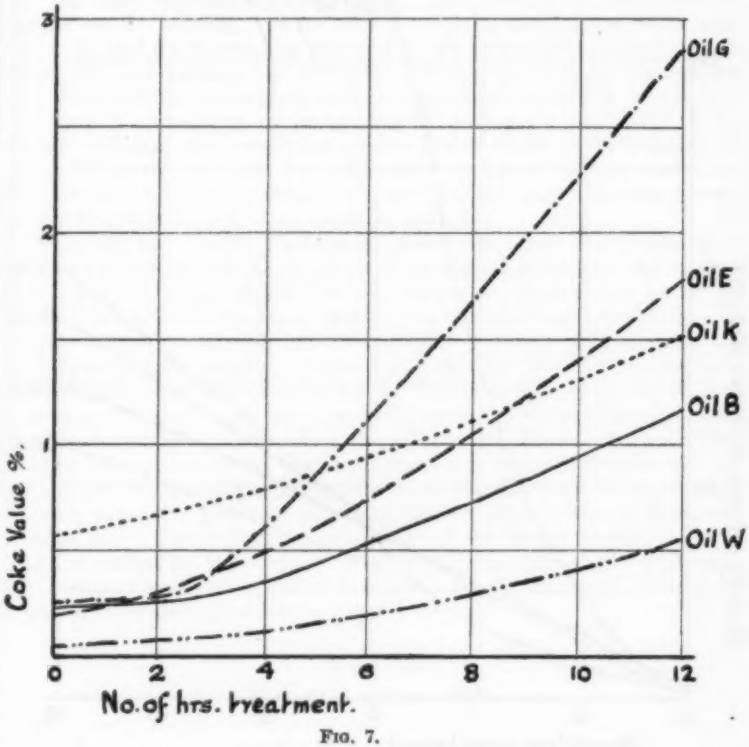


FIG. 7.

COKE VALUES OF OXIDISED OILS.

STATIC FRICTION OF THE OXIDISED OILS.

The coefficient of static friction of Oil B was measured with the apparatus previously described, at temperatures ranging from 20° C. to 110° C. There was a slight drop in the friction between 20° and 40°, but from 50° upwards there was a continued increase, most pronounced about 70°, with the result that the friction at 110° was about 5 per cent. higher than that at 20°. This curve may be considered normal for a weakly adsorbed mineral lubricating oil. On adding 1 per cent. of oleic acid to Oil B,

the friction at 20° was reduced from 0·128 to 0·110, and with increase of temperature there was a gradual decline to 0·100 at 110°. When 1 per cent. of palmitic acid was introduced, the coefficient of friction at 20° was only 0·0875, a reduction of over 31 per cent., this value falling steadily with increase in temperature to 0·057 at 110°. These results are in close agreement with those obtained in the preliminary series of tests, and

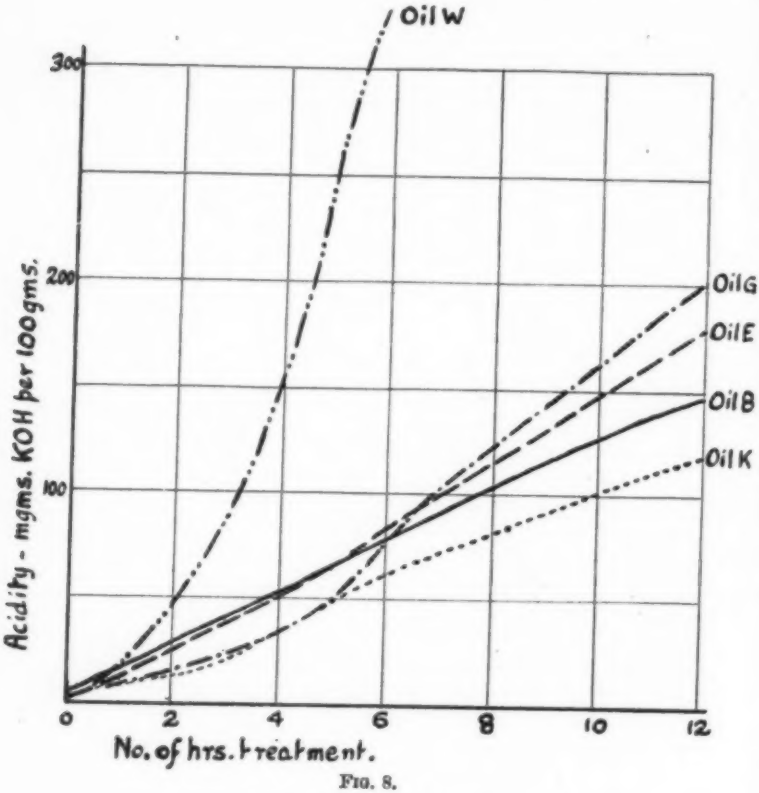


FIG. 8.

ACIDITY OF OXIDISED OILS.

clearly demonstrate that palmitic acid is greatly superior to oleic acid in respect of its power to reduce friction. Friction curves were then obtained on Oil B after it had been oxidised for 1, 2, 3, 4, 5, 6, and 12 hours. The readings on the 1- and 2-hour samples were almost identical, and slightly but appreciably below those obtained on the untreated oil, but considering that the amount of acidity in these two samples is respectively equivalent to 0·085 per cent. and 0·14 per cent. when calculated as oleic acid, the

indication is that the petroleum acids formed under the conditions prevailing during the oxidation test do not possess in any marked degree the power of reducing the coefficient of static friction of the mineral lubricating oil from which they were formed. Due no doubt to the accumulation of asphalt, amounting to 0·086 per cent., in the oil, the friction curve of the 3-hour sample was practically the same as that of the original oil, in spite of the fact that the acidity had increased to almost 0·2 per cent. calculated as oleic acid. The presence of solid asphaltic matter on the bearing surfaces caused much sticking of the slider when the 4-, 5-, and 6-hour samples were under test, particularly at temperatures below 50°, and readings were difficult to obtain, but when the temperature rose above 50° C., the asphalt seemed appreciably soluble in the oil, with the result that readings could be obtained with a greater degree of certainty, although they were appreciably above those of the original oil. After 12 hours' oxidation the difficulties increased; it was practically impossible to take any readings at all, and only in a very uncertain manner could the trend of the friction curve be indicated.

When all the asphalt insoluble in petroleum ether (I.P.T. standard) was removed from the 1-, 3-, 6-, and 12-hour samples and the friction tests repeated on the asphalt free oils, the results showed that whilst the amount of asphalt in the 1-hour sample was so small that it did not appear in any degree to influence the friction, the case was different with the 3-, 6-, and 12-hour samples. It was found that the friction of the asphalt-free oils was about the same as for the 1-hour sample at the lower temperatures, but that the friction rise with increase of temperature gradually decreased until the reverse effect prevailed in the 12-hour sample. This gradual elimination of the friction/temperature rise clearly indicates the polarity of the petroleum acids, and from the fact that a considerable increase in acidity produces only a slight reduction in the coefficient of friction, it is obvious that the orientation of the acid molecules is along, and not normal to, the surfaces on which they are adsorbed. The readings obtained are given in full in Tables III and IV, and some of the more important features are shown in Fig. 9.

TABLE III.

Static Friction Tests—Oil B.

Temp. (° C.).	Oil B.	Coefficient of Static Friction after Oxidation for						
		1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	6 hr.	12 hr.
20	0·128	0·125	0·125	0·130	0·132	0·141	0·158	0·240
30	0·127	0·124	0·124	0·128	0·131	0·136	0·149	0·240
40	0·126	0·124	0·124	0·126	0·130	0·134	0·145	0·223
50	0·126	0·123	0·124	0·126	0·128	0·133	0·141	0·190
60	0·127	0·123	0·123	0·126	0·129	0·132	0·137	0·168
70	0·129	0·123	0·124	0·128	0·129	0·132	0·135	0·163
80	0·131	0·125	0·124	0·130	0·131	0·132	0·135	0·158
90	0·132	0·127	0·125	0·132	0·133	0·134	0·136	0·158
100	0·133	0·129	0·128	0·133	0·134	0·134	0·136	0·156
110	0·134	0·131	0·130	0·133	0·135	0·136	0·138	0·155

TABLE IV.

Static Friction Tests—Oil B.

After Removing Hard Asphalt.

Temp. (° C.).	Coeff. of Static Friction after Oxidation for			
	1 hr.	3 hr.	6 hr.	12 hr.
20	0·123	0·125	0·123	0·125
30	0·123	0·123	0·123	0·123
40	0·122	0·123	0·123	0·123
50	0·123	0·123	0·123	0·123
60	0·123	0·123	0·122	0·123
70	0·125	0·124	0·122	0·123
80	0·127	0·124	0·122	0·122
90	0·128	0·127	0·123	0·121
100	0·128	0·127	0·123	0·122
110	0·130	0·128	0·125	0·122

TABLE V.

Static Friction Tests—Oil E.

Temp. (° C.).	Oil E.	Coeff. of Static Friction after Oxidation for					
		1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	6 hr.
20	0·123	0·122	0·122	0·123	0·125	0·132	0·162
30	0·122	0·121	0·121	0·122	0·124	0·130	0·156
40	0·123	0·121	0·121	0·121	0·124	0·126	0·151
50	0·123	0·121	0·121	0·121	0·125	0·125	0·145
60	0·124	0·121	0·122	0·122	0·124	0·125	0·132
70	0·125	0·122	0·123	0·123	0·125	0·125	0·129
80	0·127	0·124	0·125	0·124	0·126	0·126	0·129
90	0·129	0·125	0·126	0·126	0·127	0·128	0·130
100	0·130	0·126	0·128	0·128	0·130	0·130	0·132
110	0·132	0·128	0·128	0·129	0·132	0·132	0·133

TABLE VI.

Static Friction Tests—Oil E.

After Removing Hard Asphalt.

Temp. (° C.).	Coeff. of Static Friction after Oxidation for			
	1 hr.	3 hr.	6 hr.	12 hr.
20	0·122	0·120	0·120	0·120
30	0·121	0·120	0·121	0·120
40	0·121	0·119	0·121	0·120
50	0·121	0·119	0·121	0·121
60	0·121	0·120	0·120	0·121
70	0·122	0·120	0·121	0·121
80	0·123	0·122	0·122	0·120
90	0·125	0·123	0·123	0·121
100	0·126	0·124	0·123	0·121
110	0·127	0·125	0·124	0·120

Coefficient of Static Friction (μ).

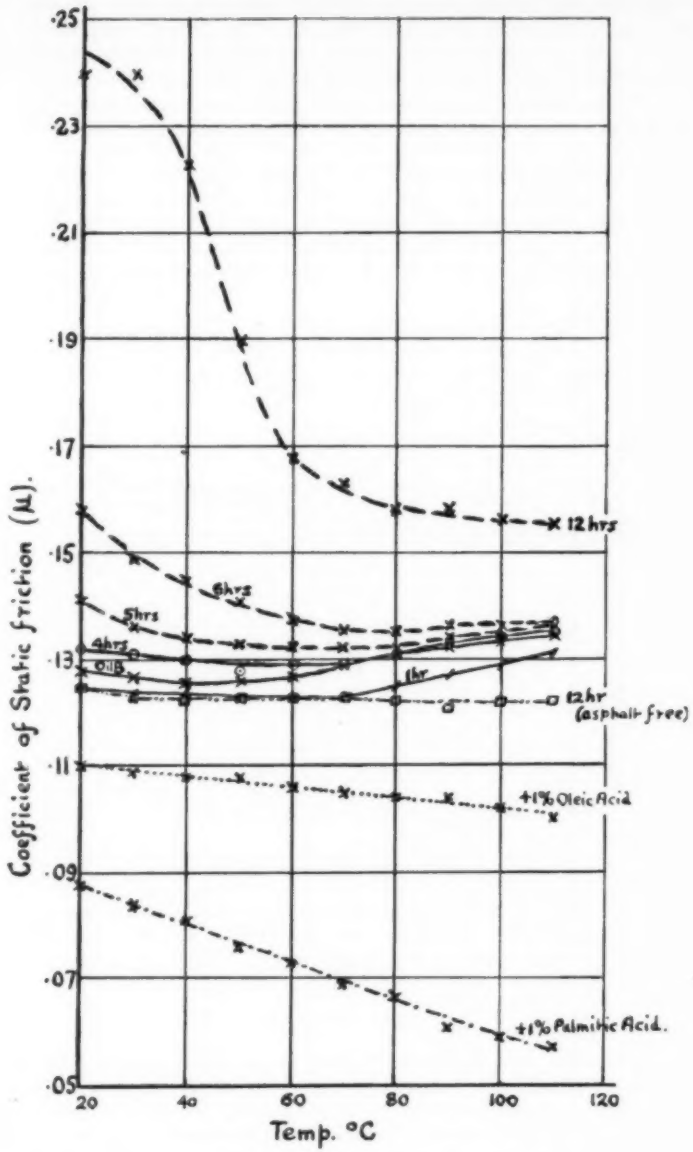


FIG. 9.

FRICTION CURVES FOR OIL B.

The friction readings for Oil E both before and after oxidation are given in Tables V and VI and Fig. 10. The general behaviour of the oil was very similar to that of Oil B, and attention need be directed only to the fact that the absence of precipitated asphalt in the samples which have been oxidised for periods of 1, 2, and 3 hours results in the friction in all cases being below the figure obtained on the original oil.

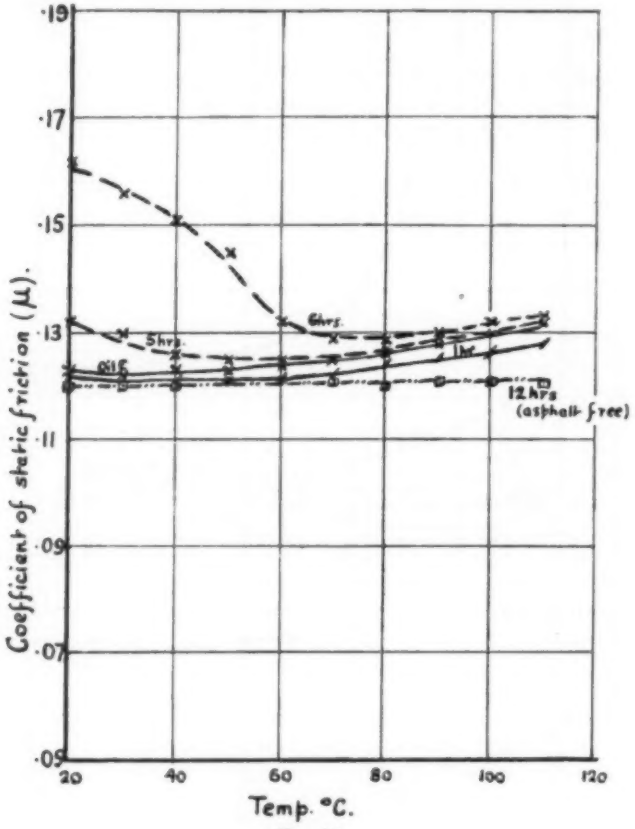


FIG. 10.

FRICTION CURVES FOR OIL E.

The friction curve for Oil G was almost flat, rising only slightly between 90° and 110°, but the addition of 1 per cent. of oleic acid and 1 per cent. of palmitic acid produced results almost exactly the same as were obtained in the case of Oil B, the former acid reducing the static friction at 20° C. by 15·3 per cent. and the latter acid by 29 per cent. After oxidising the oil for 1, 2, and 3 hours, the friction tests were practically identical, and only fractionally below the values for the unoxidised oil. After 4 hours'

oxidation the friction was slightly higher due to accumulation of asphalt in the oil, after 5 hours' treatment the readings were beginning to show uncertainty, and after 6 hours the precipitation of asphalt was sufficient to cause much sticking of the slider, particularly at the lower temperatures. As in the case of Oil B, attempts to obtain friction values after the oil had been oxidised for 12 hours were unsuccessful, and only a vague outline of the curve from 40° C. upwards could be ascertained.

There being absolutely no hard asphalt formed after 1 hour's oxidation, the asphalt was separated from the 2-, 4-, 6-, and 12-hour samples for further investigation of the frictional values. In general, the results were very similar to those obtained on the two oils previously examined, as will be noted from the results given in Tables VII and VIII, and in part shown in Fig. 11.

TABLE VII.

Static Friction Tests—Oil G.

Temp. (° C.).	Oil G.	Coeff. of Static Friction after Oxidation for						
		1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	6 hr.	12 hr.
20	0·124	0·122	0·121	0·121	0·123	0·127	0·144	>0·3
30	0·123	0·121	0·120	0·121	0·122	0·126	0·140	>0·3
40	0·121	0·120	0·120	0·120	0·120	0·126	0·132	0·3/0·25
50	0·121	0·119	0·118	0·119	0·120	0·124	0·130	0·2
60	0·120	0·119	0·119	0·118	0·119	0·122	0·130	0·18
70	0·120	0·119	0·119	0·118	0·119	0·121	0·128	0·17
80	0·120	0·120	0·119	0·119	0·121	0·122	0·131	0·16
90	0·120	0·120	0·121	0·121	0·122	0·124	0·133	0·15
100	0·122	0·121	0·123	0·123	0·123	0·126	0·133	0·15
110	0·124	0·123	0·123	0·125	0·125	0·126	0·133	0·15

TABLE VIII.

Static Friction Tests—Oil G.

After Removing Hard Asphalt.

Temp. (° C.).	Coeff. of Static Friction after Oxidation for			
	2 hr.	4 hr.	6 hr.	12 hr.
20	0·118	0·118	0·119	0·119
30	0·118	0·118	0·119	0·118
40	0·118	0·118	0·118	0·118
50	0·118	0·118	0·118	0·117
60	0·118	0·118	0·117	0·117
70	0·119	0·118	0·118	0·116
80	0·120	0·119	0·118	0·116
90	0·120	0·119	0·118	0·116
100	0·121	0·120	0·119	0·115
110	0·123	0·121	0·119	0·114

The friction curve for Oil K was characterised by the same flatness as was observed in the case of Oil G. After oxidising the oil for 2 hours, it was found that the coefficient of friction was slightly below that of the untreated oil, and practically the same readings were obtained on the

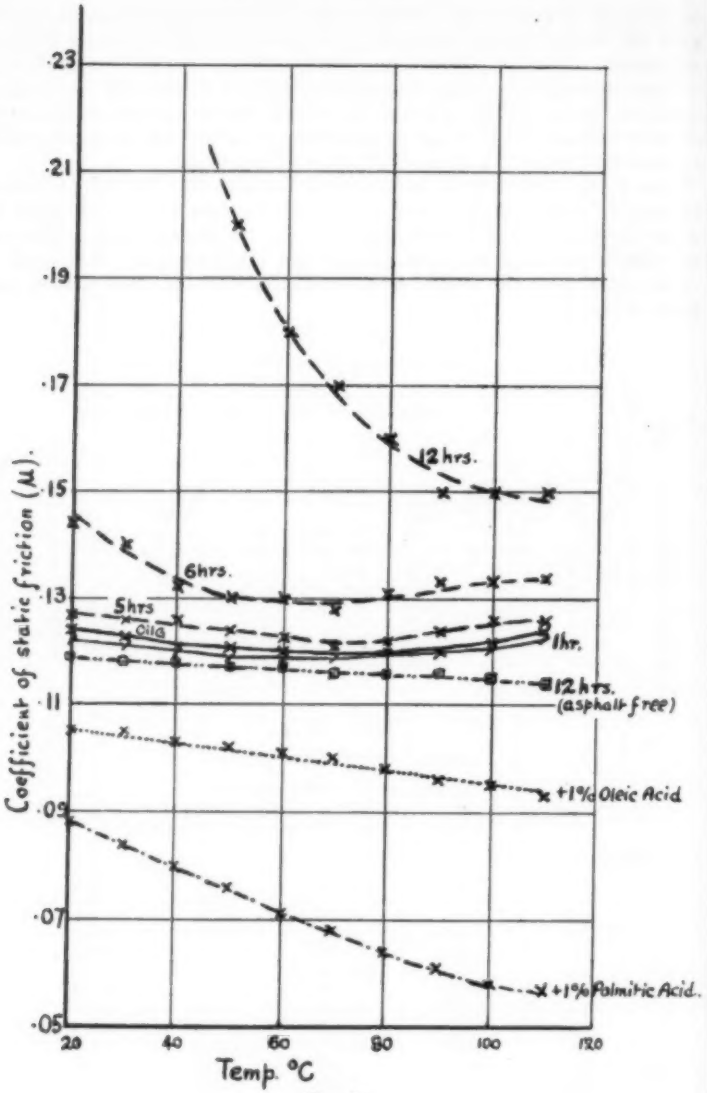


FIG. 11.

FRICTION CURVES FOR OIL G.

4-hour sample. Possibly due to thickening of the oil by tar formation, the friction at 20° C. of the 6-hour sample was slightly higher, being equivalent to the value of the original oil, but with increase of temperature

there was a steady drop, and the value at 80° C. was the same as that of the 2-hour sample. Even after 12 hours' oxidation the coefficient of

TABLE IX.

Static Friction Tests—Oil K.

Temp. (° C.).	Oil K.	Coefficient of Static Friction.					
		After Oxidation for				After Removing Hard Asphalt.	
		2 hr.	4 hr.	6 hr.	12 hr.	6 hr.	12 hr.
20	0·123	0·120	0·121	0·123	0·1255	0·121	0·1185
30	0·123	0·120	0·120	0·123	0·1245	0·120	0·1185
40	0·122	0·119	0·120	0·122	0·124	0·120	0·1165
50	0·122	0·119	0·119	0·121	0·124	0·119	0·116
60	0·121	0·119	0·1185	0·121	0·123	0·119	0·116
70	0·121	0·119	0·1185	0·120	0·121	0·1185	0·115
80	0·121	0·119	0·1185	0·119	0·121	0·1185	0·114
90	0·121	0·119	0·1185	0·119	0·119	0·1185	0·114
100	0·122	0·119	0·119	0·119	0·1185	0·1175	0·113
110	0·122	0·119	0·119	0·119	0·1175	0·1165	0·112

friction at 20° C. was only 2 per cent. higher than that of the untreated oil, and at 110° C. it was actually 3·7 per cent. less. The superior behaviour

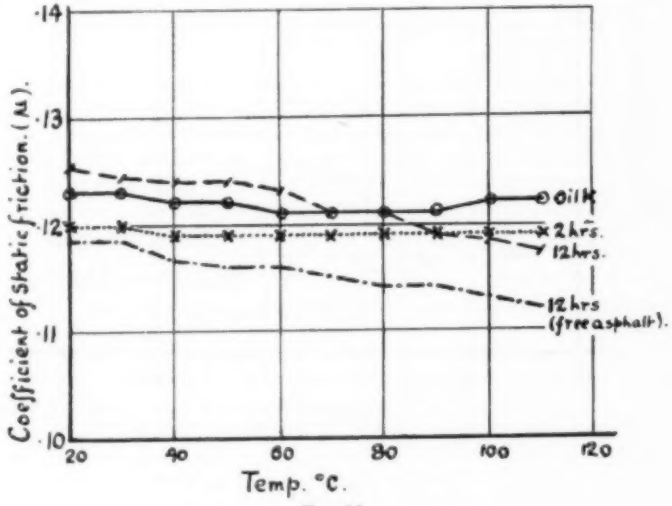


FIG. 12.

FRICTION CURVES FOR OIL K.

of the blended Oil K is in agreement with the results obtained by King,[7] and it would appear that the function of the residual stock is to provide a protecting influence which inhibits the breakdown of the acidic bodies

formed by the oxidation of the distillate oils into lower acids and asphalt. The full results are given in Table IX, and in Fig. 12 the friction curves are

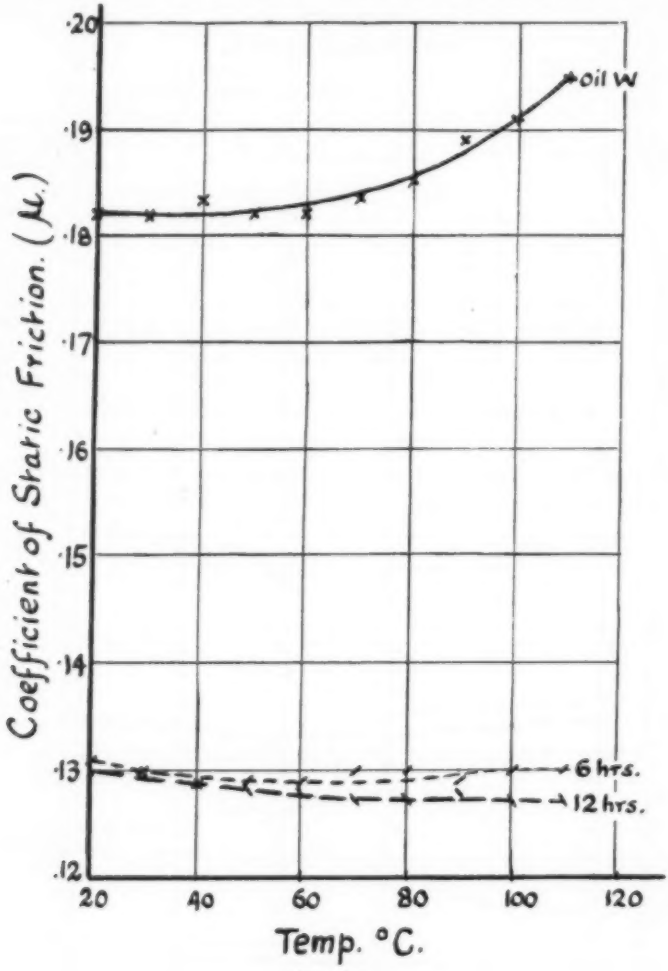


FIG. 13.

FRICTION CURVES FOR OIL W.

shown for the original oil, for the 2- and 12-hour samples and for the 12-hour sample after removal of hard asphalt.

The behaviour of the non-volatile petroleum acids is well indicated by the tests carried out on the medicinal paraffin oil (W). After 6 hours' oxidation of this oil no asphalt whatever was formed, but the acidity was

347 mgms. KOH per 100 gms.: after 12 hours' oxidation there was only a trace of asphalt, but the acidity had increased to 532 mgms. KOH per 100 gms. and the viscosity at 100° F. was 2·3 times that of the untreated oil. When the friction curves were determined, it was found that the oxidised oils were 28 per cent. lower in friction at 20° C. than the unoxidised oil and 33 per cent. and 35 per cent. respectively lower at 110° C., the results being shown in Fig. 13. Practically all drastically refined oils show a similar tendency to develop abnormally large acid values, the reason for which is not fully understood, but as the effect is liable to have most serious consequences in practice this feature should receive attention when assessing new methods of refining lubricating oils.[12]

In order to investigate the behaviour of the volatile petroleum acids, an addition was made to the oxidation apparatus by means of which the distillate coming over from the reaction tubes was condensed and collected. Oil B was oxidised for 12 hours under these modified conditions, and aqueous and oily distillates were obtained. The acidity of the aqueous portion was found to be equivalent to 39 mgms. KOH per 100 gms. of oil treated, the solution was very reactive towards copper and readily reduced silver nitrate solution; the water-insoluble portion contained acidity, equivalent to 17 mgms. KOH per 100 gms. of oil treated, was distinctly reactive to copper, but not to steel, on the surface of which it dried after 4 days at room temperature to a sticky varnish-like substance. The coefficient of static friction of this distillate when fresh was approximately 4 per cent. higher at 20° C. than that of the unoxidised oil.

Conclusions.

In view of the results obtained by Hardy, it is not surprising to find that the lower molecular-weight fatty acids do not, under boundary conditions, produce any reduction in the coefficient of static friction of mineral lubricating oils, and that the presence of polar groups alone will not impart the property of "oiliness" to a non-polar or weakly polar oil. It has previously been suggested that the difference between the effect produced by saturated and unsaturated acids is due to the difference in the length of the hydrocarbon chain, normal to the bearing surface, attached to the adsorbed polar group, and it would appear that it is this normal or effective length of the hydrocarbon chain attached to the adsorbed polar group, and not the volume of the molecule,[13] which is the true criterion of lubricating values (low coefficient of static friction). Consider A and B (Fig. 14a) to be two bearing surfaces in relative motion, each covered by spaced adsorbed molecules of lubricant; the interspaces may be filled by weakly polar molecules which are practically unorientated. Adam [14] has stated that the hydrocarbon chains attached to the adsorbed polar groups are flexible, and therefore it may be assumed that they will bend on the approach of high spots on the bearing surfaces (Fig. 14b), thereby assisting the high spots to ride over one another without metallic contact occurring. It will readily be seen that this flexibility of adsorbed molecules will be greater, the greater the normal length of the hydrocarbon chain, and it must be remembered that there are undoubtedly many degrees of secondary orientation beyond the primarily adsorbed film. This conception of

flexibility, coupled with thermal vibration, explains the extremely low value of the coefficient of friction at very low relative speed observed by Hardy in the case of palmitic acid, and in the experiments under notice dealing with the mixtures containing the higher molecular-weight saturated fatty acids. The existence of so marked a temperature effect in the friction of the mixtures containing the fatty acids was unexpected, particularly as Hardy had found that there was no temperature effect when the lubricants were pure substances. It does not seem that it can in any way be connected with the thinning of the film, although Rayleigh and Hardy both found that surfaces covered with lubricating films of infinitesimal thickness had extremely low coefficients of friction, for Hardy showed that these effects were only transitory, whereas the low values obtained

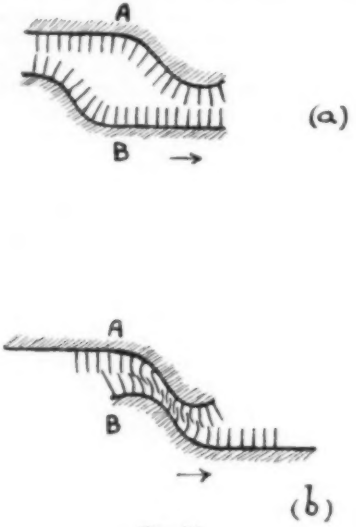


FIG. 14.

in the present case persisted for hours at the maximum temperature employed, 110° C.; the phenomenon may be attributed to greater mobility of the lubricating film due to the increase in the vibrations of the strongly adsorbed molecules.

Lubricant molecules which are weakly adsorbed will easily be displaced by thermal vibrations from the bearing surfaces, the result being an early rise in the coefficient of static friction, whereas strongly adsorbed molecules will be much more resistant to displacement. Multipolar lubricant molecules will be orientated along, and not normal to, the bearing surfaces, and for this reason their presence, whilst not appreciably reducing the coefficient of static friction, may produce a film which is very resistant to mechanical rupture. There is reason to believe that certain of the less volatile polar bodies formed by the mild oxidation of mineral lubricating oil are multipolar, and that their presence is beneficial is clearly

shown by the elimination of the friction rise with increase of temperature. Should the oxidation of the oil result in the formation of asphalt which is deposited on the bearing surfaces, an increase in the coefficient of static friction is to be anticipated, although King and Larson [15] have shown that the kinetic friction does not appear to be increased by the presence of solid products of decomposition.

In conclusion, the Author wishes gratefully to acknowledge the assistance rendered by the late Professor Gibbs, the Ramsay Laboratory of Chemical Engineering, by Dr. N. K. Adam, by the Anglo-Persian Oil Co., in permitting the use of their Stanton Pendulum machine, and by the chemical and engineering Staff of Snowdon, Sons & Co., Ltd.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Sixty-Fourth General Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, April 9th, 1935, Sir **John Cadman**, President, in the Chair.

The following paper was presented :—

THE BOUNDARY FRICTION OF OXIDISED LUBRICATING OILS.*

By E. R. REDGROVE, B.Sc., Ph.D., F.C.S. (Member).

DISCUSSION.

Dr. A. E. Dunstan pointed out that the present paper was the fourth during the history of the Institution that was concerned with the chemistry and physics of lubricating oils, and it was to be hoped that, following on the pioneer work of Sir William Hardy, the author and his colleagues would carry still further this work on the ultimate issue of lubrication. It was very much to be hoped that in the discussion there would be lines of investigation foreshadowed of which the author might possibly take advantage. What interested him particularly both in Hardy's work and in that of Dr. Redgrove was the question of so-called polarity. He thought possibly there was a tendency to ascribe too much importance to the oil itself, and not sufficient importance to the dual system of the lubricating oil and the lubricated surface. It had always to be borne in mind that a change of surface might make a vast difference to the behaviour of the lubricant. The " carpet pile " theory, which Langmuir was the first to put forward, deserved careful consideration. Such a minute amount as 0·01 per cent. of a polar body was an almost insignificant quantity of " pile." Further, he was of the opinion that recent X-ray analysis had shown that the free carbon chain attached to the polar terminal was zigzag in shape and not linear. This formation would rather militate against the yielding and mobile friction-resisting " pile."

He would also wish to direct attention to the fact that if one regarded the case of sulphuric acid, glycerol and water used in certain types of machinery it was difficult to get a consistent theory of lubrication if one had to assume a long mobile chain of atoms attached to whatever might be the active surface. He would like Dr. Redgrove's opinion as to how sulphuric acid or glycerol behaved, and what his theory of lubrication was in that case. He himself was more and more convinced that they had to regard the matter from the point of view of a dual system. He wondered,

* See pp. 612-633.

for example, whether anyone knew what happened during the running-in of a bearing in that very critical time. He supposed it was fair to assume that the two rotating or moving surfaces started out with an ordinary space lattice, but they did know that after a time they got a Beilby layer, and presumably the space lattice went, and it was difficult to say what were the points of attachment even of those polar bodies. Was it not conceivable that what one had was a colloid system in which the components actually were oil and bearing surface? This was rather borne out by the difficulty everyone found in getting the surface clean again. This suggested there was a system, and not merely a sporadic attachment of polar groups.

He congratulated Dr. Redgrove on bringing the paper forward, because it dealt with a subject upon which a massed attack of chemists and physicists in the Institution should be concentrated.

Prof. A. W. Nash, in a written contribution, said that the work described by Dr. Redgrove was of decided interest, the results obtained, so far as boundary lubrication was concerned, being in general accord with those of other investigators.

The coefficient of friction–temperature curve of the medicinal paraffin oil W is especially interesting, since Hardy found that B.P. medicinal paraffin showed no increase in the coefficient of friction with temperature (for the range 18–106° C.), the oil, on that account, being used as a blending diluent in his work (see D.S.I.R. Lubrication Research Technical Paper No. 1, p. 10, etc.). Could the author express any opinion on the cause of this divergency?

The curve (Fig. 3) correlating molecular weight and friction coefficient for the unsaturated acids, suggested from its shape that unsaturated acids higher than erucic acid might conceivably show still greater friction-reducing power. In this connection it would be interesting to know whether the author had any information on the comparative behaviour of the high melting-point stereo-isomers of oleic and erucic acids, namely, elaidic and brassidic acids. Their different spatial molecular arrangement might conceivably lead to a different value for the friction coefficients.

In connection with the improvement in friction coefficient shown by the oxidised oils, attention might be drawn to results obtained by the Alox Chemical Corporation in the U.S.A.

These people find that unusually good friction-reducing properties are exhibited by certain oxidation products from petroleum oils and waxes. The oxidation was carried out under pressure at temperatures between 100° and 150° C., catalysts being used if desirable, and the non-volatile saponifiable portion was removed and used for doping commercial lubricants. It was believed that these saponifiable bodies comprised cyclic esters, lactones and anhydrides of high molecular weight carboxylic and hydroxy acids (cf. U.S.P.'s 1,690, 768–769, 1,863,004, 1,895,374, and Alox booklet).

With reference to the theoretical aspect of the lowering of the static frictional coefficient, attention might be directed to some interesting work by Rhodes and Lewis in the U.S.A. (*Ind. Eng. Chem.*, **1934, 26**, 1011). Using a similar type of apparatus (" 3-ball " slider moving on chromium-

plated bearing studs) these investigators concluded that the rise in friction coefficient with temperature of a Penna oil was due to an oxidation process. They found that certain organic compounds, notably β-naphthol and *cyclo*hexanol, were capable of lowering the friction coefficient of the oil to an extraordinary degree, especially in the neighbourhood of 100° to 130° C. At these temperatures the friction with 0·05 per cent. blends was reduced to a minimum, in some cases increasing rapidly after this point. No satisfactory explanation could be offered; although the compounds were certainly polar, their chain length would be very small indeed.

These investigators suggest that the repression of the decrease in "oiliness" on heating may be due to the action of addition agents as negative catalysts in the oxidation of the oil. They claimed that this hypothesis was supported by the fact that most of the substances that have beneficial effects were known to act as anti-oxygens. The author of the present paper had shown, however, that repression of the decrease of "oiliness" on heating may be brought about by oxidation of the oil, which was supported by the Alox Chemical Corporation patents. Could the author, therefore, express any opinion on the possible reconciliation of these two points of view?

Mr. J. Kewley, in a written contribution, said that it would be very desirable to have further confirmation of the views expressed by the author and others as to the distribution of the molecules in the surface film relative to the surface, and the relation of length and perhaps other dimensions of the molecules to the coefficients of static friction. A new method of obtaining definite evidence as to the structure of the surface film was now available, *i.e.* the electron diffraction method. He understood that Professor Finch and his colleagues at South Kensington had already done some preliminary work in this direction, which appears to support the views generally held. Mr. Kewley suggested that this method opened out a probably useful field of research in this connection. Interesting in themselves as these questions were, they, however, play a minor part in the practical problems of lubrication, as engineers rightly design bearing surfaces so as to avoid as far as possible the risk of developing the very dangerous boundary lubrication conditions.

Col. S. J. M. Auld described Dr. Redgrove's paper as one which provided a great deal of food for thought. He had some difficulty in commenting on it owing to a change in his own views on the subject during the last six or eight months. After hearing Mr. King's paper at the beginning of 1934 he, like a great many other people, had been prepared for a particularly big advance in the theory of lubrication. The effect of oxidation on lubrication appeared to offer an explanation of many of the difficulties encountered in practice at high temperatures, though even at that time he had not regarded it as necessarily being a bridge to ordinary conditions. Even if one accepted seizing temperatures as being a measure of lubricity in the sense of Herschel's definition, King's work still left them groping for an explanation of the effect of oxidation under more ordinary conditions where boundary lubrication might come into play. This, he took it, was what Dr. Redgrove was giving

them a line on at the moment. What Dr. Redgrove had really done was to show that if ordinary lubricating oils were oxidised the friction in the first place was definitely increased. But if the asphalt so formed were removed the friction was reduced. This effect was ascribed to other residual oxidation products, supposedly actual acids, and, according to Dr. Redgrove's hypothesis, acids definitely polar in character. The effect was not very marked, and he found it somewhat difficult to line this up in his own mind with his conception of the Air Ministry work and with the work of Rhodes and Lewis published in 1934, which he presumed was what had been alluded to in Professor Nash's remarks. He knew nothing personally about Rhodes and Lewis, but their conclusions appeared sound and the work emanated from a reputable source. It was made quite plain by these investigators that in their opinion a paraffinic-base oil properly purified actually lost in value by oxidation. Curiously enough, that effect was most marked round about the temperatures where maximum total effect on the oils examined had been noted by Dr. Redgrove, namely, around 70° to 75° C. No reference had been made to this increase in friction being due to the accumulation of any other bodies, as, for example, asphalt. Was it not rather significant in Dr. Redgrove's work, when he began to get a lot of asphalt formation, which of course made determinations very difficult, that at the higher temperatures where re-solution took place the curve came down again? Was it not possible that in the asphaltenes, or whatever actually formed them—asphalteneogens they might be described—was the solution of the problem, and not necessarily in the acids at all? Would it not be interesting, for example, to take the oils that had been oxidised, measure their coefficients of friction, get rid of the hard asphalt by precipitation, wash them out with caustic soda, and then see what the coefficients of friction were? Quite likely, if this were done, indications would be found of some sort of colloidal material acting as a layer, as Dr. Dunstan foreshadowed, instead of the present conception of chemical compounds of simple polar nature such as had been ascribed to the acids formed. It would be interesting to see how this actually worked out, and he would like to hear Dr. Redgrove's views on the suggestion.

Professor J. S. S. Brame said there were one or two points on which he would like a little information beyond those already referred to. Col. Auld had mentioned the question of asphalt and its probable colloidal condition. When they had those very interesting photographs, on the lines of Hoblin's work they were down to quantities of asphalt in the neighbourhood of 0·047 per cent. and there was a perfectly clear disc. He took it from the context of the paper that that referred to what was technically known as hard asphalt, and its removal probably meant the oil had been treated with I.P.T. specification naphtha. Was "hard" asphalt the right material to consider? Was it not more probable that it was the oxidation product commonly known as soft asphalt, and not "hard" asphalt?

An assumption appeared to be that the acid products of oxidation were the progenitors of this form of asphalt. The author was not very definite on the point, but seemed rather to question it himself. There was perhaps

not much evidence of it. A point which was of special interest, and which tied up with what Col. Auld had said, was that in the precipitation of the asphalt during oxidation a colloidal substance was involved. If that were so, might not the formation of these acids by oxidation be the cause of the precipitation of the asphalt?

Dr. F. B. Thole said that among the many points of interest in the paper he would restrict his comments to a few. Fig. 10 showed that the rise in friction coefficient only began to be noticeable when asphalt particles commenced to separate from the oil and then presumably began to adhere to the metal surfaces. If, therefore, the conditions could be so adjusted that the asphalt particles were "peptised" (that is, existed in a very much smaller state of division than normal), it is probable that the surface tension effect would tend to prevent their adhesion to the metal and retain them suspended in the oil. It was interesting in this connection to note that when asphalt was precipitated by petroleum ether from a used motor-engine oil, the state of subdivision of the asphalt particles was much greater in the case of a compounded oil than in the case of a straight mineral oil.

Reference to the curves in Fig. 4, which indicated the rate of increase in asphalt with time of oxidation, showed that great caution must be exercised if such curves were used to assess the relative stabilities of oils. In the cases quoted the relative stabilities of the oils B, E and G were in different order at the two-hour, four-hour and six-hour stages, and Professor Fachini had shown that still further changes in "order of merit" were liable to occur if the oxidation period were prolonged still further.

The very potent effect of palmitic acid in permitting gentle slip of the slider at an exceedingly small angle of inclination was striking, but the phenomenon emphasised the importance of the load factor in assessing friction-reducing qualities. While palmitic acid is very effective at light loads, a point will be reached, if the load is steadily increased, when carbon tetrachloride, sulphurised oils and other "extreme pressure lubricants" will outstrip palmitic acid in effectiveness. It would seem that "polar bodies" do not afford as yet a full explanation of boundary lubrication phenomena.

The reference to asphalt being formed by the breakdown of acidic bodies into lower acids and asphalt hardly seems to be substantiated by evidence. Acids are only one product and form, in fact, a somewhat insignificant proportion of the total products of oxidation, for the amount rarely exceeds 1 per cent., while considerably larger amounts of aldehydes, ketones and probably alcohols and lactones are simultaneously produced. It is equally justifiable to assume that some of these are the parents of asphalt, while it would seem still more probable that asphalt is a polymerisation product containing oxygen and not a breakdown derivative.

Mr. W. E. Gooday said it was a matter for regret to all who had been trying to keep the petroleum industry straight that palmitic acid—rancid palm oil—did the trick. One point to which other speakers had referred more theoretically was not quite clear to him. Dr. Redgrove had encouraged him to think he was going to give a complete explanation of the question of the cylinder stock acting as an inhibitor, but he still failed to understand the

suggestion that Dr. Redgrove made. He would have thought that the heavier products, usually considered as being less stable than the distillates, would contribute rather more to the total products of oxidation. Was it a fact that, taking into consideration Dr. Thole's description of the sum-total of oxidation products, they would have the same type of curve that Dr. Redgrove had shown for his asphalt tests?

Another point on which he would like to hear Dr. Redgrove express an opinion was in regard to the wax content of oils, to which reference had recently been made in the D.S.I.R. Lubrication Research Technical Paper No. 2.

He was a little disappointed to hear Mr. Kewley's remark that the paper was not of sufficient practical importance. It had struck him in reading it through that this was a paper particularly of theoretical interest, but written and presented from a rather more practical point of view than was characteristic of many of the more theoretical contributions.

Mr. E. A. Evans said he felt that the paper had dispelled from their minds some of those perfectly ridiculous ideas about using an oil of almost any quality. It was very clear that during the first hour or two a process of oxidation occurred. During this time the coefficient of friction was somewhat reduced, but after that the coefficient of friction was greatly increased. That was really the essence of the paper. It was all it was intended to show. It automatically followed from the results given that there was absolutely no correlation whatever between the coke values, the acidity, the asphalt, or the friction. It just showed the oil was getting worse and worse. He was very interested in the figures which had been shown concerning the blended oils containing cylinder stock. Many people had advocated the use of straight distillates, but he did not think anybody had continued to use them. After all, practically all the oils one met on the market, except spindle oils, were blends. He did not think they could get away from them, and there was plenty of evidence here in support of them.

Regarding Dr. Dunstan's remarks, if orientation did not take place on a surface it was a little difficult to understand the so-called breaking-in of an engine or the running-in period. He had great difficulty in understanding how a very thin oil functioned during these two periods. He also had great difficulty in believing that the very thin oils which were being advocated in the United States were the ideal lubricants for a new engine. They might be all right when the engine was being motored round, but he could not see that they were the proper oils to use when the car was put on the road. Something thicker must be used, otherwise there would be a tearing away of the surface. The idea of a pile and the bending over of molecules did afford a working hypothesis, but we are up against the difficulty of understanding how a perfectly inflexible material like graphite could possibly react if we accept the working hypothesis.

Mr. P. Docksey asked if Dr. Redgrove could give a figure for the repeatability of his apparatus. One could see from points on the curves in Fig. 2 that if the slider was cleaned and covered with oil, and a series of tests made, the results were repeatable to within 1 per cent. He would like to know what was the repeatability if, after an experiment had been

made on a certain oil, the apparatus was completely cleaned and the oil again tested. This repeatability, which was a measure of the effectiveness of cleaning and the ease with which a certain type of surface could be repeated, was the crux of the whole thing as far as this type of apparatus went.

Another point was with regard to preparing the surface of the slider. He gathered that it was not given a polished surface, as was usually done in experiments of this type (*e.g.* Hardy's experiments), but had a matt finish.

With regard to what Dr. Redgrove had said as to the superiority of a blended oil, it would be much more conclusive if they could have figures for, say, a bright-stock blended 140 grade oil and a straight-run 140 grade both from the same crude. The superiority of the blended oil (oil K in the paper) might well be due to the fact that it was of Pennsylvanian origin.

Professor J. S. S. Brame asked what was the actual minimum angle of tilt at which the sliding of the slider could be detected.

Captain R. O. King, in a written communication, said that Dr. Redgrove's experiments show that *after* somewhat severe oxidation mineral oils are better lubricants in the boundary conditions selected than when fresh. The view that lubricating value improved because of the development of acidity was not supported by the journal-bearing experiments described in 1934 (J.I.P.T., 1934). Thus Russian No. 1, one of the oils used in the journal-bearing experiments, and similar to Dr. Redgrove's Oil B, was deleteriously affected in respect of seizing temperature by more than a mild degree of oxidation, and seizing temperature may be taken as indicating the advent of boundary conditions. The hypothesis advanced in respect of journal-bearing lubrication was that oxidation *activity* is the factor required to raise seizing temperature, and it was found that an oil on standing tended to lose the extra lubricating value gained previously while oxidation was in progress. Therefore, in practice, fresh oils would be capable of improving in lubricating value for a life period depending on the nature of the oil, whereas used oils would necessarily be inferior in this respect. On the other hand, if Dr. Redgrove's experimental results could be applied to practice, it would appear to be an advantage to start using thoroughly oxidised oils from which the asphalt formed in the process had been removed.

Boundary friction, in Dr. Redgrove's experiments, is measured on the surface of adsorbed molecules if we accept the assumption made, for example, by Hardy and Nottage, that the spherical slider penetrates to that surface and a thickness of two molecules only separates the metals of the plate and slider. It is physically impossible to bring two metal *surfaces* uniformly into such close contact by any known method of surface finishing, and it is apparent, with a little consideration, that the degree of contact mentioned need not and is unlikely to occur at any moment of time at more than three points. Therefore the type of friction measured in the experiments of Dr. Redgrove, or in those of Hardy and Nottage, can prevail at any time on an infinitesimal part only of surfaces in relative motion. That is, on point contacts which in practice would continually appear and then vanish into tiny surfaces as the main surfaces rubbed together. There-

fore the oxidation or other characteristics of what may be called point contact friction or true adsorbed layer friction cannot be applied to practice, that is, these characteristics cannot be used to predict the probable performances of lubricating oils, in a journal bearing, for example.

The journal-bearing friction measurements already mentioned were made in conditions of practice, the parts being of engineering dimensions. Separation of the heavily loaded metal surfaces was maintained at temperatures extending to 300° C., while the friction remained extremely small, coefficients as low as 0·0005 being observed on many occasions. The characteristics of the friction were not those of the fluid type and seemed to be explained most readily by the hypothesis that a relatively thick boundary *layer* was formed between the mono-molecular layer adsorbed on the surface and the completely fluid layer which tended to squeeze out as the temperature exceeded 200° to 250° C., depending on the viscosity of the oil. Thus it appears possible to obtain a boundary state in practice, but the friction is measured on the surface of the relatively thick layer and the characteristics of the effect seem to be related to the oxidation characteristics of the oil.

Dr. E. R. Redgrove, in reply, said he thought the justification of his paper was indicated by the wealth of discussion it had aroused, and he felt that an apology was due to the Institution for the fact that although the work described was completed four years ago, he had not had an opportunity to prepare the work for presentation before that evening.

Replying to Dr. Dunstan, he said that although 0·01 per cent. of palmitic acid was a minute amount to cause the friction of Oil W to be reduced from 0·182 to 0·14, it must be remembered that Oil W was practically acidless and only weakly adsorbed. The addition of 0·01 per cent. of palmitic acid produced frictional and acid values comparable with those of refined mineral lubricating oil of about equal viscosity.

Considering the space arrangement of the carbon bonds it was natural to assume that the hydrocarbon chains attached to the polar groups would, in dilute solution, take the form of a curved zigzag spiral, and there was no reason to assume that such a configuration would militate against their flexibility, especially if they were spaced in a weakly or non-adsorbed fluid medium.

That sulphuric acid and glycerol functioned as lubricants in certain types of machinery was due to the fact that practically any fluid, or for that matter any gas, would act as a lubricant if it did not enter into chemical combination with the bearing surfaces and if it were possible to ensure that the journal could be kept floating in the bearing without actual contact occurring between the surfaces whilst they were in relative motion.

Although the formation of a Beilby layer destroyed the space lattice, the influence of the underlying structure might still be manifest at the surface. Even if it were not so, the electrical difference between metal and lubricant would still exist and so ensure orientation.

Professor Nash referred to the friction-temperature curve of Oil W. The rise in friction with increase of temperature was entirely unexpected and received very close study. It must be assumed that the difference between Hardy's findings and those of the author was due to the dissimilarity of the

surfaces and the design of the apparatus. The curve in Fig. 3, correlating molecular weight of added fatty acid with coefficient of friction, is, in the case of the unsaturated acids, drawn through only three points, because other unsaturated acids of guaranteed purity could not be procured at the time; were other points obtainable it would most likely be found that the curve had a sweep similar to that of the saturated acids. From purely theoretical considerations it would appear that the question of stereoisomerism would not at high dilution effect friction-reducing properties.

Some of the experiments described in the paper indicated that the lower oxidation products of lubricating oil would have high frictional values, and whether the friction of a lubricating oil is raised or lowered by oxidation would depend very largely upon the conditions. In the practice of lubrication, adequate ventilation of all circulating systems was essential to ensure that the more volatile oxygenated decomposition products were removed. Observations by the author indicate that the reducing action of the lower oxygenated compounds often plays an important part in the decomposition of lubricating oils, and the beneficial results obtained from many negative catalysts may be ascribed to inhibition of the reducing reaction referred to above.

Replying to Mr. Kewley, the author said he much regretted that at the time his experiments were being conducted he was unaware of the investigations of Professor Finch, whose work he (the author) believed had already shown the collapse of the "pile" at elevated temperatures. It would be interesting to know whether the collapse was due to excessive thermal vibration or direct chemical union.

Colonel Auld had raised an interesting point because, although the manner in which the asphalts were precipitated in the experiments was bound to increase static friction, there was evidence in practice (to quote only one example, the skin on a Michelle thrust bearing) that a colloidal layer might be beneficial to lubrication, and it was most desirable that the function of such layers should be further investigated.

Professor Brame was correct in assuming that the "hard asphalt" referred to in the paper was obtained from the oxidised oils by treatment with I.P.T. specification naphtha. Investigation of the oxidised oils showed that "soft asphalt" was a very elusive product and would appear to be the petroleum acids themselves, possibly polymerised to some extent during isolation. The very slow movement of the slider in the friction experiments occurred at an angle of inclination of 1° 36′.

Dr. Thole had drawn attention to the curves in Fig. 4; the author was in complete agreement with his remarks and had already drawn attention to this matter (*Petroleum Times*, 1934, **32**, 583). Cases had come under notice in which the early rate of formation of asphalt had not been maintained, generally traceable to faulty refining or accidental contamination. Extreme-pressure lubricants would appear to derive their special properties from the inclusion of some substance—*e.g.* sulphur, chlorine, etc., which so contaminated the bearing surfaces when metallic contact occurred that actual welding was greatly retarded.

The reducing action of the lower oxygenated products of decomposition has already been referred to and it would appear that these bodies obtain a certain amount of the oxygen which they require from the more oxygenated

acids already present, whilst condensation of the molecules deprived of their oxygen formed asphaltic compounds. Should the oxidising test be carried out in the presence of a strip of copper, it is found that in a short space of time the presence of copper can be detected throughout the body of the oil and after several hours' treatment copper mirrors can sometimes be detected on the sides of the reaction tubes.

Replying to Mr. Gooday, it must be remembered that the cylinder stocks are much less volatile than the distillates and that generally speaking only small quantities of hard asphalt are formed from them during their oxidation. Naturally different methods and conditions may show different results, but when employing the method of oxidation used for the tests under discussion it is generally found that the asphalt formed from a blend is less than might be expected from the oxidation test of the constituent distillate and bright stock. Unfortunately, he (the author) had not done any work on the influence of wax, but it was evident from the report of the D.S.I.R. Technical Paper No. 2 that the question had an important bearing on the behaviour of a lubricating oil.

Mr. Evans once again shows his complete knowledge of the difficulties which beset those who attempt to solve any of the problems attaching to lubricating oils and the practice of lubrication. The action of graphite may be explained by the substitution, under extreme boundary conditions, of metal to metal friction by graphite to graphite friction, thereby providing a greater margin of safety, the value of which cannot be ignored. Further than this, lubricating oils are stated to spread and to be orientated better on a graphite than on a metal surface.

Mr. Docksey asked for the figure for the repeatability of the friction apparatus. Generally speaking duplicate tests agreed within 2 per cent., but this limit was obtained only after the polished surfaces had been abandoned in favour of the matt finish. This finish was found to be perfectly satisfactory with the three-point contact apparatus, but it might not work well with the single spherical slider of Hardy's apparatus.

Captain King seemed to have drawn conclusions from the paper which were not justified by the results, for on referring to Figs. 9 and 11 it will be seen that the reduction in boundary friction brought about by twelve hours' oxidation (after removing the hard asphalt which had been formed) was nothing like so great as that caused by the addition of 1 per cent. of palmitic and oleic acid to the unoxidised oil. The less volatile petroleum acids formed by oxidation of the oils are weakly polar bodies and their presence is beneficial although the advantage so derived may be more than outweighed by the presence of other products of decomposition. Fig. 12 clearly demonstrates the importance of chemical stability. Again Captain King assumed the existence of a mono-molecular film between the bearing surfaces—which assumption is not justified unless the quantity of oil present is only sufficient to supply such a film. The stability of an adsorbed film of lubricant is not necessarily connected with its properties of reducing friction under boundary conditions, and resistance to seizing is more likely to be due to properties such as are imparted by extreme-pressure lubricants.

THE EFFECT OF THE PRESSURE IN THE PROCESS OF CRACKING.

By M. S. Nemtzov.*

One of the basic conclusions derived from the investigation carried out on a large experimental scale with the liquid-phase cracking process, worked out by Leslie and Potthoff [17] and by Sachanen and Tilicheev,[1] is the fact that the pressure has no substantial influence on the process and the character of the products obtained. It is true, if the cracking process is carried out mildly, and considering the inaccuracy of the method used for analysing the complicated mixture of hydrocarbons obtained, that it is difficult to notice the changes in the composition of the petroleum products.

Nevertheless, the data obtained lately, mainly as a result of theoretical investigations carried out with individual hydrocarbons, are in contradiction with the above conclusions.

In so far as the problem in connection with the quality of the cracked gasolines is one of the most important in the development of cracking, a discussion in the light of the latest published literature data, as well as of the special investigations carried out in the High-Pressure Institute, may be of some interest. Let us analyse the problem methodically, covering the quantitative and the qualitative sides.

(1) The Formation of Gases and the Yields of Gasoline.

As far as can be ascertained from the results of a number of investigations undertaken for the purpose of investigating the mechanism of the thermal decomposition of hydrocarbons,[2, 3] the primary reaction occurring in the destruction of the hydrocarbon chain is of the monomolecular type. Consequently, the pressure, *i.e.* the concentration of the reacting molecules in the reaction zone, should not affect the velocity of cracking, as stated by Sachanen and Tilicheev.

Some authors are of the opinion that an increase in the pressure prevents gas formation because of a greater "symmetry" of the splitting of the hydrocarbon chain, *i.e.* because of the splitting off of short fragments at the end of the chain.[4, 5]

However, on the basis of the conception of the spontaneous character of the thermal decomposition, as well as from the point of view of the radical theory,[41] such a conclusion does not seem to be sufficiently justified.

The increase in the formation of gases usually observed in the course of the cracking of hydrocarbons under atmospheric pressure should be rather ascribed to the following phenomena :

It should be kept in mind that the realisation of the process in the vapour

* Government High-Pressure Institute in Petrograd. Translated by A. A. Boehtlingk. Paper received September 24th, 1934.

phase requires, because of the poor conductivity of the vapour phase, a considerable degree of over-heating of the walls of the chamber. The individual molecules, after contacting for a considerable period with the wall, are apt to suffer a large degree of decomposition, whereby gaseous products are mainly formed. Thus, in this case, the pressure will play only an indirect rôle, and as a matter of fact it may be replaced, for example, by a change in the construction of the furnace, which would do away with an excessive over-heating of the walls. The latter fact particularly can be credited to the up-to-date vapour-phase cracking units (Gyro and De Florez).

A direct effect of the pressure is noticed in the increased yield of gasoline instead of gases, because of the condensation reactions taking place with the unsaturated gaseous hydrocarbons formed in the course of the process. This includes in this particular case the lower olefins and di-olefins.

The homogeneous polymerisation of these hydrocarbons is a bimolecular reaction,[6, 7, 8] the velocity of which is proportional to the concentration of the reacting molecules, *i.e.* to the square of the pressure.

Moreover, the velocities of the polymerisation of the olefins[8, 9, 10] and of the di-olefins[7] decrease with the increase in their molecular weights. Thus, the gaseous unsaturated hydrocarbons will yield products of a medium molecular weight on being cracked in the liquid phase. These molecules will have a low tendency to a further polymerisation. The impossibility for their heavy polymerisation is derived from the equilibrium conditions existing in the polymerisation–depolymerisation processes.[8] It should also be noted, as was shown in the investigations carried out by R. Pease,[6] as well as in those undertaken in the High-Pressure Institute,[8, 10, 11] that the velocities of the homogeneous polymerisation of olefin hydrocarbons are comparatively low, and that they would not be able, under the liquid-phase cracking conditions, to effect a marked decrease in the gas formation.

However, in the case of condensation processes being carried out directly in the zone of formation of unsaturated hydrocarbons under ordinary cracking conditions, these velocities may prove to be considerably higher. This is concluded from the fact that the fragments of the decomposed molecule carry initially the entire energy of activation of the decomposition, *i.e.* about 60,000–70,000 calories.[2, 3, 12, 13] Accordingly, each of the newly-formed molecules carries an average of about 35,000 calories, *i.e.* an energy which is sufficient for the accomplishment of a condensation reaction[6, 8, 10] at the first collision with another molecule able to be condensed.

In the case of a noticeable sub-atmospheric pressure, when cracking at atmospheric pressure, the probability of a collision of such an "active" molecule with another unsaturated molecule will be slight, and then, instead of a polymerisation, a deactivation of the "active" molecule will occur in its first collision with the walls. In the collision of a charged molecule with the hot walls there is a possibility of a severe cracking, down to methane and carbon.[10] However, under pressure the probability of a collision of molecules among themselves increases at the ratio of the square of the pressure, and the above phenomena can be practically eliminated.

The above possibilities for the most probable mechanism of condensation during cracking lead also to the conclusion that the following conversion

of the removed cracked gases into gasoline by polymerisation is of a lesser advantage, with respect to the velocity of the process, than if the condensation process were carried out directly in the zone of cracking.

(2) The Stability of Cracked Gasolines.

In so far as the stability of the cracked gasolines is probably primarily connected with the presence of unsaturated hydrocarbons with a conjugated double bond, a higher stability should be expected with products low in these substances. As we know from the work carried out by S. N. Lebedev and others,[7] the highest ability for thermal polymerisation is also characteristic for the hydrocarbons with conjugated double bonds. Therefore these hydrocarbons will be easily removed from the gasoline fractions by the above method.

The above data on the bimolecular character of the polymerisation processes may be applied also in this case,[22] *i.e.* under the conditions of super-atmospheric pressure of the liquid-phase cracking process, the concentration of the di-olefin hydrocarbons in cracked gasolines must be many times lower, and the gasolines accordingly more stable.

The theoretical conclusion is entirely confirmed in practice, and it is evidently the principal distinction between the cracking process carried out under super-atmospheric pressure, and without it.

However, from the practical standpoint, this point should not be considered as being of any particular importance, because in selecting the corresponding refining method (for example, refining by hydrogenation [14]), this disadvantage of the vapour-phase cracking could be easily eliminated.

(3) The Anti-knock Properties.

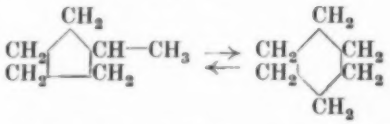
The most important practical and theoretical problem is that of a possible influence of the operating pressure during cracking on the anti-knock properties of the gasoline. The importance of this problem is emphasised in connection with the application of severe types of vapour- and liquid-phase cracking (re-forming), for the preparation of "premium" gasolines with a high octane number.

Inasmuch as the aromatic and the aliphatic hydrocarbons with side-chains are the active anti-knock carriers, we shall discuss the genesis of these compounds under the conditions of cracking.

Referring now to the aromatic hydrocarbons, two possibilities for their formation during cracking may be mentioned, namely: (1) by dehydrogenation of the naphthenes, and (2) by the synthesis of the aromatic ring from the unsaturates. Unfortunately, we have not sufficient knowledge on the mechanism of these conversions of hydrocarbons under the conditions of ordinary cracking, and therefore we may discuss these possibilities only with reservations.

Referring now to the first type of reactions, it should be noted that at elevated temperatures the rôle of the dehydrogenating catalysts can be played to a considerable extent by the walls of the reaction vessel, and there is no reason to assume that the splitting of hydrogen is a homogeneous process, which has very little probability in this case.[15] Moreover, it may

be assumed that the formation of aromatic hydrocarbons during cracking is possible not only from the hexamethylene rings with a predetermined structure (they should not have two chains attached to one carbon atom of the ring), as would be required for the catalytic dehydrogenation by the Zelinskii method. Under the conditions of cracking, there is a possibility for isomerisation even of the five-member ring into a six-member ring, the latter being then able to be dehydrogenated. Such an isomerisation cannot be avoided at a sufficiently long exposure of the hydrocarbon in the reaction zone, because the state of equilibrium [42] is here doubtless present for the reversible reaction of the type :



and inasmuch as the hexamethylene hydrocarbons will be subjected to a further transformation into benzene hydrocarbons, the reaction will proceed continuously in the right direction.

The only conditions for its efficient performance will be a sufficient velocity, which could probably be attained by the use of the simplest catalysts, such as a special material used for the walls of the reacting vessel. Unfortunately, there are almost no reports on this type of catalysis, in spite of the possibility of applying directly and immediately all the data from the cracking process.

Referring to the influence of the pressure existing in the reaction zone in this process, it is possible to mention only the partial pressure of the components of the reaction, namely, of both types of hydrocarbons and of hydrogen. Thus, the pressure of the latter could be able to shift the equilibrium of the reversible dehydrogenation reaction towards the hydrogenation, and in that case there would be a decrease of the octane numbers of the gasoline, accompanied by a decrease in the content of aromatics.

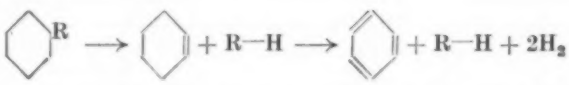
However, the experimental data on the equilibrium of the hydrogenation of quite a number of aromatic compounds obtained most recently in the High-Pressure Institute,[16] indicate that at a low concentration of the hydrogen in the cracked gases and a high temperature of the reaction zone in the vapour phase, as well as in cracking at super-atmospheric pressure, the equilibrium is almost entirely transferred towards the dehydrogenation, and consequently in both cases the conversion of the naphthenes into aromatic hydrocarbons may proceed practically at the same intensity.

Referring now to the effect of the pressure on the *velocity* of dehydrogenation; generally speaking, in this case, the vapour-phase cracking may have some advantages. Thus, if we accept the presence of the heterogeneous process, then there may be a possibility for a kinetic magnitude below one, and even of the magnitude of zero. In this case in the vapour-phase process, where the catalysing surface per unit of weight of the raw material is higher, the dehydrogenation may proceed at a higher rate.

However, under the conditions of high temperatures, and in the presence of the simplest catalysts, the zero magnitude is hardly possible, and it will probably be nearer to one.

Particularly, if we select the proper material for the apparatus, the process could probably be realised in the above manner [44]; then there would be no advantages left in the vapour-phase cracking. The experimental checking of these assumptions has already been started in the High-Pressure Institute.

In addition to the dehydrogenation reaction, the hexamethylene hydrocarbons are probably able to enter into quite characteristic reactions of "de-alkylation," whereby tetra-hydro products are formed, which rapidly lose the remaining four hydrogen atoms and are converted into aromatic hydrocarbons according to

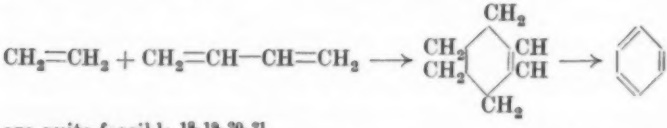


This type of conversion, which was foreseen by Jones and Wheeler,[43] has unfortunately not been investigated more closely, but it is obvious that if the reaction proceeds homogeneously, then it must be of the monomolecular type. In the case of the presence of a heterogeneous mechanism of the reaction, all the above assumptions should be applied to hydrogenation.

Thus, in the genesis of aromatic hydrocarbons from naphthenes, the influence of the operating pressure should either be unnoticeable, or it may be reduced to a minimum by selecting the proper catalytic effect.

The effect of the pressure is less evident in the synthesis of aromatic hydrocarbons from unsaturated compounds.

Unfortunately, there are no reports in the literature about direct investigations of the kinetics of these processes, and it is possible to judge on the formation of aromatic hydrocarbons only by indirect data. On the basis of these data, we may say that, considering the remote possibility for the scheme of Berthelot (condensation of acetylene) under the comparatively low temperatures of cracking, and because of the insignificant concentrations of acetylene possible under these conditions, the possibilities for a mechanism of polymerisation of olefins and di-olefins



are quite feasible.[18, 19, 20, 21]

The conversion of *cyclo*hexene (or of its homologues) into an aromatic hydrocarbon should not present any particular difficulties in this case, because the obtained hydrocarbon, which has a less stable structure, will have, as was indicated above, the thermodynamic tendency to proceed towards dehydrogenation at any of the pressures used in cracking. Therefore, it is sufficient to investigate the first phase of the above mechanism—namely, the condensation of the olefin with the di-olefin.

Being a homogeneous bimolecular reaction (although there are no direct indications to that effect in the literature, but because of the fact that the reactions of the homogeneous thermal polymerisation of olefins,[6, 8, 10] di-olefins,[7, 22] and acetylene [23] are bimolecular, there is no reason to assume

another mechanism in the given case), this process, assuming the other conditions to be identical, should proceed at a higher velocity with an increase of pressure in the reaction zone; and if it is possible, in the case of vapour-phase cracking, that the olefin or di-olefin molecule, on being contacted with the over-heated wall of the chamber, is subjected to de-activation or to severe cracking (here the catalytic action of the wall is also possible in the latter direction), then under the pressure the probability of a collision with the wall will have less chance to occur, because of the effective collisions which take place in the formation of aromatic hydrocarbons. However, the probability of active collisions accompanied by the formation of other compounds (for example, olefins and di-olefins) will be given not by the total pressure, but by the relative concentration of various types of hydrocarbons in the reaction zone.

Thus, if we accept the above reasoning—the composition of the mixture of hydrocarbons, as well as the other conditions as being equal—then the process which is carried out under pressure will cause the formation of aromatic hydrocarbons to proceed more successfully.

However, the composition of the reaction products obtained on cracking under pressure may be different from that obtained on cracking without pressure. Unfortunately, here also the experimental material is meagre, because the vapour-phase process was usually investigated under high temperatures and the liquid-phase process under low temperatures (the re-forming process is of a recent date), and in consequence the comparison of available data is difficult. Therefore, here also only an assumption can be made; namely, that the influence of the pressure may be shown in the lowering of the concentration of unsaturated hydrocarbons, because of the retardation of the dehydrogenation reactions with the aliphatic hydrocarbons.

If the dehydrogenation of the aromatic hydrocarbons, as mentioned above, is not susceptible to low partial pressures of hydrogen, then the olefins and the di-olefins are in a different position. According to thermodynamic calculations [24, 25, 16] and experimental data,[26, 27] already at low hydrogen pressures the hydrogenation of olefins proceeds to a great extent, and consequently, kinetically quite feasible reactions, such as the splitting of hydrogen from the *iso*-paraffins,[28, 29] when cracking under pressure, will proceed to a considerably smaller extent (particularly with the low molecular hydrocarbons).

At the present time, it is difficult to predict the magnitude of this type of reactions under conditions of cracking, and therefore definite conclusions on the influence of the pressure on the genesis of aromatic hydrocarbons from olefins and di-olefins cannot be reached. However, we may assume that they are of no great importance. Thus, for example F. Fischer and H. Schrader,[30] on the basis of an analysis of literature data,[20] as well as on the basis of their own investigations, conclude that in the pyrolysis of petroleum products and of individual paraffins, it is possible to obtain only 5–7 per cent. benzene, and they indicate other ways for explaining the formation of aromatic hydrocarbons in the coking of coal.

If we compare these data with the extremely low yields of aromatic hydrocarbons at the temperature of the pyrolysis, even when using a special raw material, we may reach the conclusion that the synthesis of

benzene hydrocarbons from products of severe cracking is evidently not the leading reaction in the formation of aromatic hydrocarbons.

The considerable difference in the chemical composition between the products of the vapour- and liquid-phase cracking, as mentioned above, is evidently due primarily to the difference in the temperature conditions. Thus, the ratio of the amount of di-olefin hydrocarbons to olefins in the vapour-phase distillates is considerably higher than in the liquid-phase cracking, because the temperature coefficients and the energies of activation of the condensation are much lower with the di-olefins (di-olefins: $E = 17{,}500$–$25{,}000$ calories,[7, 22] olefins: $E = 35{,}000$–$38{,}000$ calories [6, 10, 8]). Therefore, in the high temperatures, the condensation reactions of olefins among themselves are accelerated to a greater extent, as is the case with di-olefins, which, generally speaking, are polymerised with considerably greater ease.

As has been shown, the energy of the activation of the reactions of thermal decomposition is expressed by about 65,000 calories, whilst the condensation reaction does not exceed 38,000 calories. Thus, on increasing the temperature, the velocities of the formation of decomposition products increase at a considerably higher rate than those of condensation products, which is the cause of the accumulation of a considerable amount of unsaturates. Moreover, as was also mentioned above, at high temperatures there is a possibility of the shifting of the equilibrium conditions of the polymerisation reactions, because some of the hydrocarbons can be depolymerised to quite a considerable extent under the cracking temperature conditions (for example, the tri- and tetra-*iso*butylenes are converted into di*iso*butylene [31]).

Thus, as a result of the analysis of the possible directions of the action of the pressure on the genesis of aromatic hydrocarbons, we may say that there is probably no basis for any quantitative data in favour of cracking without pressure.

Referring now to the higher content of aromatics in vapour-phase cracked gasolines and in the products of pyrolysis, this can be ascribed to a considerable degree to the fact that, as a result of a more severe decomposition of the raw material thermally the more stable, the aromatic hydrocarbons are mainly accumulated among the products left undecomposed after the high-temperature cracking. All the other hydrocarbons are either completely cracked or subjected to a heavy condensation, accompanied by the formation of heavy tars and coke, and are thus eliminated from the final product.

Referring to the second type of hydrocarbons, which produce the high anti-knock properties of the liquid fuel—namely, the aliphatic hydrocarbons with branched chains—it is worth mentioning that at present there is an absence not only of data on the mechanism of their formation, but even of methods for their quantitative determination in gasolines. Only after a systematic investigation of the detonation properties of individual hydrocarbons was it found that this class of hydrocarbons is the most valuable component of the motor fuel, and quite a number of laboratories began to pay particular attention to this very important problem.

It is hoped that from the research initiated in this direction in the High-Pressure Laboratory by S. E. Livshitz and V. L. Moldavskii a quantitative

method for the determination of *iso*-paraffins will be developed, and then the investigator will have a valuable tool for the investigation of the genesis of branched aliphatic hydrocarbons in the processes of cracking, hydrogenation, and re-forming. So far, it is only possible to assume, on the general basis of the mechanism of pyrogenetic decomposition, that the pressure will increase considerably the efficiency of the process of formation of *iso*-compounds.

As a matter of fact, parallel with the possible but less probable process of isomerisation of the normal paraffin hydrocarbons into *iso*-paraffins, attention is directed to the unavoidable process of consecutive decomposition reactions and the polymerisation of olefins, which, according to the elementary statistics, must lead to the formation of a branched hydrocarbon skeleton. This successiveness of the reaction is emphasised by the fact that the thermal resistance of the unsaturated hydrocarbons of an average molecular weight is considerably below that of the corresponding paraffins,[32, 33, 34] and the unsaturated condensation products of the olefins are again subjected to decomposition, and at a higher rate. Of still greater importance for the isomerisation process in the re-forming is probably the peculiarity of the mechanism of the homogeneous olefin polymerisation. As was shown experimentally,[6, 8, 10] only one out of hundreds of active collisions leads to the formation of condensation products. The majority of the quasi-molecules of the polymer formed in the first moment are dissociated again because of the accumulation of an excess of energy in the latter (the energy of activation plus the heat of reaction), whereby there are formed either transient molecules, or molecules having a structure different from the first ones.

In the latter case, because of the consecutive reactions of decomposition and condensation, statistically there must be an accumulation of branched chains.

In the extreme case, because of the short periods of time between the splitting of the bond and the condensation with the same fragment of the molecule, a pure isomerisation will take place. However, under the comparatively severe conditions existing in cracking, a complete decomposition is more probable. It will be accompanied by the formation of preferably two olefin molecules, which, being present in the active state, because of the stored energy of activated decomposition (see above), will immediately react with other unsaturated molecules. The velocities of these bimolecular reactions will increase rapidly with the pressure.

Thus, on the basis of the theoretical conceptions, we may predict that in re-forming under pressure, the amount of the *iso*-compounds in the gasoline should be greater than on re-forming the same raw material at the same temperature and duration, but under atmospheric pressure.

An indirect confirmation of this conclusion may be seen in the data by I. Albright[35] and W. Goldtrap,[36] who showed that when increasing the operating pressure in the re-forming, there is an increase in the octane numbers of the gasoline. Unfortunately, the absence of the chemical characteristics of the gasolines does not permit a complete check of the conversion mechanism in the illustration cited in the article.

However, as far as it is impossible to expect an increase in the content of aromatics through increase in pressure, as was shown above, the increase in

the octane numbers can probably be explained by the isomerisation process. This permits of making the assumption that in the preparation of an anti-knock fuel it is not advisable to promote the formation of aromatics, and every attempt should be made to promote the formation of *iso*hydrocarbons accompanied by a minimum of decomposition.

As a result of the latter, great losses may occur through the formation of gases. But the decomposition of *iso*-paraffins and *iso*-olefins may even lead to a lowering in the octane numbers, because a relative accumulation of aromatic hydrocarbons may prove to be unable to compensate the losses of the highest anti-knock components—namely, the hydrocarbons with branched chains.

In conclusion, it may be said that considering the assumptions derived from the theoretical reasoning in this article as being confirmed to a great extent by special investigations, particularly by the investigations started in the Government High-Pressure Institute, we may be able to state that the basic processes for the preparation of highly anti-detonating gasoline obtained by severe cracking must be either the re-forming under pressure or the destructive hydrogenation, the latter being some kind of a more severe re-forming process carried out in the presence of hydrogen.

Referring now to the vapour-phase cracking, this type of cracking is probably to receive a special character of a high-temperature process with strongly specialised problems for the production of di-olefins, probably as by-products. Upon a further development of the pyrogenetic processes, the latter should receive a better theoretical foundation than the pyrolysis of petroleum raw material, with its insignificant yields in finished products.

Such processes may be the destructive hydrogenation of naphthalene, raw anthracene, higher phenols from primary tars from various solid fuels, etc.[37, 38, 39, 40]

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

RUMANIAN BRANCH.

A GENERAL MEETING of the Rumanian Branch of the Institution of Petroleum Technologists was held on February 16th, 1934, when the following paper was presented:

COMPLETIONS OF WELLS.

By J. L. CHAILLET (Member).

Many of the points discussed in this paper are dealt with only from the point of view of Rumanian practice, and therefore may not be applicable to other fields. Although some of the items deal with the period between the drilling of the well and the commencement of production, they do not necessarily apply to the actual bringing-in of the well. The subject has therefore been dealt with from two standpoints: Organization and Technical.

ORGANIZATION.

Before the actual drilling of a well is commenced, a detailed working programme for its completion should be prepared, and full consideration should be given to the lay-out of the site, not only for the drilling period, but also for the longer and more important production period.

The preparation of a working programme involves:

a. An estimate of the drilling programme and the anticipated production from the technical viewpoint.

b. An estimate of the cost of drilling and the cost of production, together with an estimated value for the crude oil and gas produced and the products to be obtained therefrom.

c. An estimate of the capital expenditure to cover both the drilling and the production periods, minus the value of recoverable assets.

d. An estimate of the depreciation on all plant to serve as a basis for completing the estimate under *b*.

The decision to drill a well should be based on the net result of the estimates, due consideration being given to such matters as the prospects of production being obtained, the time required for the production to be remunerative, the merits of other locations under consideration, and the possible trend of oil prices.

By careful estimation of the above factors it is possible to arrive at a decision as to whether a location should be developed or whether the completion of a well should be postponed or even abandoned, depending on its condition.

The various items to be considered in preparing the above estimates should include:

a. All operations during what is known in Rumania as the drilling programme (*program de lucru*), with detailed data regarding the weight of strings of casing at their depths of setting; the type of drilling mud and the estimated quantities required; the quality and quantity of cement; the types of casing and cementing shoes and baffle plates; the details of perforated casing; whether mechanical or electrical coring and deviation measurements are required; the details of tapered tubing if it is to be used; whether snubbing operations are necessary; and whether provision is to be made for washing and swabbing.

b. The cost of the items under *a*, including figures for:—

1. Drilling Costs:—
   Direct drilling expenses,
   Auxiliary services (water and power),
   Depreciation,
   General expenses.
2. Production Costs:—
   Direct lifting expenses,
   Auxiliary services,
   Depreciation,
   General expenses.

If the figures under 1 and 2 are totalled and the amount under *c* (capital expenditure less recoverable) is added, the result is an estimate of total expenditure during the life of the well. The grand total can then be compared with the estimated value of the products to be obtained, deducting any royalty and taxes. By substituting different values, high, medium or low estimates of possible profit can be arrived at.

As a result of these detailed estimates, which should be accurate to within 5 per cent., decisions can be made on various points, such as the surface to be occupied and the roads required; the details of the necessary lines for steam, water, etc.; the power plant needed; and other accessories such as pumping plant, separators, meters, etc. A scheme for the ordering and transport of all materials and equipment can also be drawn up.

While this serves as a basis for an organized time-schedule to avoid delay, the arrangement must remain flexible and ready to meet any emergency which might arise.

Technical.

Assuming that work has proceeded according to schedule and that drilling operations could normally terminate within a fortnight, there still remain various matters to be prepared for the proper completion of the well.

Liner or Oilstring.—The diameter of the liner is more or less fixed by the diameter of the preceding string of casing. Its length can be estimated, and an extra 20 to 30 metres should be ordered.

The perforated portion of the liner can be decided only when full information is available as regards the thickness of the sands and the various beds which are to be cased by the liner. Generally, it is good practice to use small perforations or slots opposite sands which are known to give trouble during the production period. Many small perforations are preferable to a few large ones.

For 4- to 5-inch diameter liners, four rows of perforations will suffice, without excessive weakening of the pipe, if they are located at vertical distances of not less than ten times their diameter. For 5- to 7-inch liners, five or six rows are sufficient, and for 7- to 9-inch liners, eight to ten rows.

Where no serious sand troubles are expected, it is good practice to select the size of the perforations in accordance with the formations penetrated. This facilitates the cleaning of the annular space between the liner and the borehole, and also permits the production of oil from narrow sands contained in marl beds. An electrical log will give valuable information as to the length of pipe required for each type of perforation, and it is advisable to have a few lengths of perforated pipe in reserve. The rough edges of holes or slots should be filed off smooth.

Liner is usually run on a coarse-threaded left-hand nipple, by which it is attached to the drill pipe for lowering. The unscrewing of the liner is a matter of some importance, and will be considered in detail.

Few troubles are experienced in setting liners at depths of less than 1000 metres, provided that the nipple has been tested when hanging in the table and has been made up just hand-tight with a chain tong before lowering.

A case is known where right-hand threaded landing nipples, four threads per inch, are used, and it is to be hoped that these will never cause the liner to drop prematurely into the hole.

Nipples which unscrew with a slot device are not to be recommended for any hole above 1000 metres in depth, or for a hole which is crooked at the bottom.

Even when a well-designed nipple is used, difficulties can occur when unscrewing the liner. These may be caused by the application of too much weight or by the liner turning too freely in the open hole. For deep holes, the lowest joint of the liner should be provided with two small fish-tails at the bottom to bite into the formation when the liner is turned. By this means the coarse-threaded left-hand nipple will unscrew more easily.

Another point regarding the unscrewing is that the liner and the drill pipe on which it is lowered do not bend equally. If a joint of blank pipe is added above the nipple, the unscrewing becomes almost a certainty.

Tubing.—A considerable amount of material has been published about tapered tubing, and the discussion of the results of its application in Rumania could fill a paper itself. In regard to flowing wells, there is still much to be learnt as to the size and length of each string of tubing. For wells which have to be pumped or produced by gas lift, the problem has a different aspect from the start. For flowing wells there is always a doubt as to what the daily average production and the gas-oil ratio will be for, say, 80 per cent. of its ultimate recovery.

If one surmises correctly, then the resulting gas economy by the use of tapered tubing is theoretically appreciable. In the prevailing circumstances of flowing wells, with paraffinous oil in the majority of cases, more importance should be given to the fact that the tubing chosen should almost guarantee that the well can clean itself properly before being considered as completely in production than to a possible theoretical gas economy. If it is desired to consider both items as of equal importance, it is recommended to possess a snubbing device and to equip the well for swabbing. But both, snubbing and swabbing, are operations which should be applied only in emergencies, as being cumbersome and not without danger in high pressure wells.

The use of too small a tubing for the cleaning stage of a newly-completed well may necessitate frequent circulation with fresh oil to prevent a small shot of mud clogging the tubing.

The Author considers that swabbing is an unsafe method, but if it is used, it is preferable to apply it in combination with frequent oil circulation and by-passing of gas in the casing. The safest method of bringing-in a difficult well is to rock it with a mixture of gas and oil in the casing and tubing simultaneously. Thus the conditions of natural flow are imitated, causing no disequilibrium on the strata and avoiding application of *extra* pressure on the beds such as is unavoidable when it is necessary to use circulation when the tubing is obstructed with mud or other material, as may be the case with swabbing. Also, there is no escape of gas of unknown duration or force, and the well and its surroundings remain perfectly clean.

If the well has to be snubbed, the lower part of the tubing, equal in length to the length of the liner, should have collars tapered down and up, to ensure easy lowering and extracting. Also, the upper part of the tubing, of the same length, should have smoothed-off collars, in order to avoid damage to the rubbers of the snubbing device.

All tubing for pumping wells and for snubbing should be controlled as to its internal diameter, and the making up of doubles helps to save time.

It is essential that the time between the last circulation on the bottom with the bit, prior to running the liner or production string, and the moment when the mud can be thinned down with the tubing fitted on the tubing head and the Christmas tree in place, should be as short as possible.

The shortening of this period depends on such factors as the depth and nature of the well, the conditions of the mud, and the state of the plant required for use. The initial construction of the derrick should have taken into account the easing of operations during this period, and also the possibilities of replacing the mud by water and water by oil. The presence of a neighbouring well with gas at casing pressure would assist in accelerating the coming-in of the new well. All the preparatory work to ensure a shortening of the bringing-in time is of great importance. In case these preparations are not fully terminated, it is preferable to continue mud circulation, with the bit on the bottom, rather than to pull out with the knowledge that future operations would not run smoothly.

When the liner is being cemented, the disadvantage of the completed hole standing during the setting of the cement must be taken for granted.

In some cases the plug and baffle plate are drilled out with a diamond-point bit on the tubing, in order to lessen the time required if this is done by the use of drill-pipe of a smaller diameter. Except when such drill-pipe is not available, it is safer to use the drill-pipe method than tubing. The water channels of the bit, when used on the tubing, may become a menace during the production period, and tubing is not suitable for drilling or for milling. The presence of such a bit would moreover make it impossible to measure bottom-hole pressures and temperatures during the production-period of the well.

Christmas Trees.—Various types of Christmas tree are available, and safety and flexibility are the main features of the more elaborate devices. It is the opinion of the Author that in many instances, particularly when the last water-shut-off may be doubtful, it is necessary to have two high-pressure side outlets at the casing flanges.

Separators.—Separators are placed either near the well or grouped, and in some fields both systems are in use. The advantages of the group system are: simplified supervision; only one manifold required for oil and one for gas; less lighting required than for individual separators; close proximity to lease tanks; and the reduction of the number of separators, since the reserve can be calculated for the whole group.

The disadvantages of the group system are that, with a wide well spacing, the lines become long and must be buried; the possibility of wax deposition and the inability to use a go-devil; the lines must be of larger diameter in order to allow for the wells not declining at the same rate; extra steam lines are necessary; no reduction can be made in personnel unless the wells can be left without a watchman all the year round. Also, when the tubing pressure of a well drops to the allowable minimum, it will be necessary to connect that well to an individual separator at the well-head in order to prolong its flowing life.

It would therefore appear preferable to place the separator near the well, as high as possible, and of easy access for handling.

Meters.—Oil and gas meters are still considered to be a luxury on wells, and yet regular measurement is of great assistance and adds to efficiency. On State lands in Rumania two measuring tanks per well are compulsory. If a good oil meter was used, one tank would suffice, and in some cases only the general main tanks would be required.

The results obtained over the last three years with a British-made oil meter and oil-level controllers are so satisfactory that one would expect them to be in greater use, particularly as they are comparatively cheap. Gas meters, although still a luxury with many operators, have now conquered their field in general.

If the oil is metered on each well, it should be possible, by using the gas-trap pressure, to transport both gas and oil through their lines direct to the gas plant and the main pump station, thereby eliminating internal measuring tanks and pump stations.

The accuracy of oil meters is within the limits of tank measurement, and one has a complete check of the quantity. Their upkeep is a simple item of routine, as is the case with orifice meters for gas.

In conclusion, it is suggested that the film may assist in describing field practices. It would be a great advantage to the oil industry in

general if properly directed films of technical operations could be shown. Such films would be better than any description, and possibly more instructive than a journey, if grouped in sequence and elucidated with graphs and charts where necessary.

DISCUSSION.

Mr. Gwyn Elias said that the crisis in the life of a well was the period between the moment when the bit entered the oil strata and the time when the well entered into normal production.

In wells completed at depths of 2000 metres and having high pressure, the mud pressure is the key to satisfactory completion. Mud is necessary to keep a well under control when drilling-in, and the question arises as to what damage the mud does. In America it is suggested that sands can be mudded off almost simultaneously, but this is a debatable point. There is also some doubt as to whether the use of a thick mud would prevent oil issuing from the sand.

During the last few years it has been customary to produce a well from two or three horizons simultaneously. From observation of several wells it appeared that, while one or two horizons were open, the third, probably the lower, was not open. It seems reasonable to assume that any mud settling in the hole would tend to close off the lower sand, and it is usually this sand which is the most powerful as regards yield and pressure. He desired to ask the Author's opinion regarding the starting up of a well which was intended to produce from a number of horizons simultaneously.

Mr. Biermann said it was important to note that, when comparing costs, it would be found that in most countries they do not tally so closely.

Mr. Boaden said that Mr. Chaillet had mentioned that wells completed with one string of casing appeared to give more uniform results than those in which a liner had been run. He would like to know the reason for this.

With regard to wells producing simultaneously from two horizons having different pressures, he asked whether the horizon having the lower pressure would fail to produce until the other horizon had dropped to the same pressure.

Mr. Chapman asked the reason for the practice in the Gura-Ocnitei field of raising the separators as high as the fourble board when the receiving tanks were in the valley below the well level.

Mr. Crooks stated that it was essential that drilling mud, as well as being of the requisite weight, should have its viscosity maintained within certain limits.

He also stated that a compound for maintaining the weight of the mud had been discovered in Rumania.

Mr. C. McF. Leitch, referring to the financial estimates, asked if the results proved to be higher or lower.

Mr. J. L. Chaillet, in reply, said that the type of mud used certainly had an effect on the activity of a well. In general, a thick mud would plaster off better, but would give slow progress, apart from requiring higher pump pressure. Thin mud was preferable in virgin territory, but in known territory it was better to use a thick mud.

It has been suggested that the addition of barytes was harmful to completion of a well, but he had found no proof of that.

In reply to Mr. Biermann, he regretted that he had no details of current costs of other countries.

In regard to Mr. Boaden's remarks on the one-string programme, one is more limited in the event of an unforeseen occurrence. When using a one-string programme any mishap to the casing is enough to endanger the well. Whereas, when two strings are in use, it may be necessary to cut only one string, and repair the well safely.

If there is any indication that one sand, in a well producing from two horizons, is not yielding production, it is preferable to make a special washing to prepare the low-pressure sand for later production. A test should be made by hanging the tubing below the upper sand, allowing the well to produce through the tubing from the lower (high-pressure) sand, and then open up the low-pressure sand, by letting it produce temporarily through the casing.

In reply to Mr. Chapman, the placing of separators at a height was to take advantage of the topographical situation. The case quoted by Mr. Chapman has caused some comment in oil-circles.

On the question of the financial estimates, Mr. Chaillet said that the results might be just as easily higher or lower. Unforeseen difficulties or troubles would increase costs, while better progress than anticipated would effect considerable saving. With a certain amount of experience and knowledge of conditions, the estimates could be correct to within 5 per cent. For wells of an explorative character, however, it would be impossible to estimate the costs within so small a limit.

IMPROVED METHODS OF EXAMINING MINERAL OILS, ESPECIALLY THE HIGH BOILING COMPONENTS.

By J. C. Vlugter, H. I. Waterman, and H. A. van Westen.

SYNOPSIS.

A new method is given for analysing hydrocarbon oils of the type of lubricating oils. The results of the analysis are given as: percentage aromatic rings, percentage naphthenic rings, percentage paraffins (free paraffins and paraffinic side-chains). The analysis is effected without any chemical or physical separation between groups of hydrocarbons.

Aromatic rings are determined from the change in physical constants on complete hydrogenation, naphthenic rings and paraffins from the properties of the completely hydrogenated oil.

Because a large number of oils have been examined by the Authors, actual hydrogenation has become superfluous, as the constants of the completely hydrogenated oil may be predicted from those of the original oil. Only molecular weight, refractive index, density, and aniline point need be known to calculate the composition of an oil.

Introduction.

The structure of the individual hydrocarbons contained in lubricating oils and other mineral oils of high molecular weight is very complicated, so that these compounds cannot be considered as the simple representatives of a certain group, *e.g.* paraffin, naphthene, or aromatic. The amount of aromatic *compounds* which it is possible to remove from the oil with the aid of concentrated sulphuric acid is no more a true measure of the aromatic character of an oil. One should think of Pennsylvania oil, a typical example of a paraffinic oil, from which a considerable part can be removed with sulphuric acid. Therefore, according to the Authors' opinion, it is much better in the case of high-boiling oils to determine the amount of aromatic *rings*, naphthenic *rings*, and paraffinic side-chains (eventually free paraffins). This so-called ring analysis might be compared to the well-known practice of determining sulphur *content* instead of the amount of sulphur *compounds*.

To illustrate the above, one should imagine the compound ethyltetrahydronaphthalene, $C_{12}H_{16}$, which is neither a pure aromatic nor a pure naphthene. In fact, this compound should be considered as being a mixture of an aromatic ring, a naphthenic ring, and a paraffinic side-chain. Then one comes, for instance, to the composition C_6H_4,C_4H_7,C_2H_5; in other words, this compound contains 48 per cent. (by weight) of aromatic rings, 34 per cent. naphthenic rings, and 18 per cent. paraffinic side-chains.

Because aromatic and naphthenic rings may be present together in one molecule, a separation of the molecules is of no use. Sulphuric acid, which separates the oil into a group of high aromatic ring content and a group without or of low aromatic content, has no value for the ring analysis. Instead of a separation, chemical or physical, the Authors carry out a

complete hydrogenation of the aromatic rings present. In this way these rings are converted into hydroaromatic or naphthenic rings. An oil which originally consisted of aromatic and naphthenic rings with paraffinic side-chains after complete hydrogenation consists only of naphthenic rings with paraffinic side-chains. The amount of hydrogen consumed during this hydrogenation is a measure for the aromatic ring content. The ring analysis of a mixture of naphthenes and paraffins has been dealt with extensively in a preceding paper.* Nevertheless, from remarks by several readers, the Authors are aware that this method has not always been clearly understood by some investigators. The analysis of aromatic free oils is of essential importance for the examination of oils containing aromatics. The principles on which the method for analysing aromatic free oils was based will be summarised below. For details the publication mentioned should be consulted.

Analysis of Aromatic Free Oils.

When the carbon and hydrogen content of an aromatic free oil—that is, a mixture of naphthenes and paraffins—and the molecular weight are determined, the elementary composition can be calculated, and then the average number of naphthenic rings per molecule is known. If, further, a definite type of naphthenic rings is assumed, the percentage by weight of naphthenic rings can be calculated. For instance, if for a saturated hydrocarbon mixture there is found an average molecular weight of 450 and a hydrogen content of 13·59 per cent., the composition of this oil is $C_{32\cdot4}H_{60\cdot9}$, and the average series formula C_nH_{2n-4}. In other words, this oil is on the average tricyclic. One might represent it as perhydroanthracene with one or more paraffinic side-chains. If one side-chain is assumed to be present, then, in ring structure, there is $C_{14}H_{23}$, and as paraffinic side-chain $C_{18\cdot4}H_{37\cdot8}$. The calculation of the elementary composition from the C/H ratio can be omitted if Fig. 1 is used. In this figure the hydrogen contents of the different hydrocarbon series have been plotted as a function of the molecular weight. Curve 1 gives the hydrogen content of the paraffins C_nH_{2n+2}, curve 2 for the monocyclic naphthenes C_nH_{2n}, curve 3 for the dicyclic naphthenes C_nH_{2n-2}, etc. For a hydrogen content of 13·59 per cent. and molecular weight 450, point P is found on the curve of the tricyclic naphthenes.

The method described above has a disadvantage, because for an accurate ring analysis the utmost precision is required when carrying out the elementary analysis. Therefore the Authors do not carry out any elementary analysis, but determine the specific refraction $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ of the saturated oil, which is the same. In fact, for saturated hydrocarbons there is a linear relation between the hydrogen content and the specific refraction. This fact may be elucidated by the following. From the work of Eisenlohr † on a number of pure compounds the atomic refractions of the C and H atom for different wave-lengths of the light are known. For the wave-length of

* J. C. Vlugter, H. I. Waterman, and H. A. van Westen, *J.I.P.T.*, 1932, **18**, 735–750.

† F. Eisenlohr, " Eine neue Berechnung der Atomrefraktionen L," *Z. physik. Chem.*, 1910–11, **75**, 585.

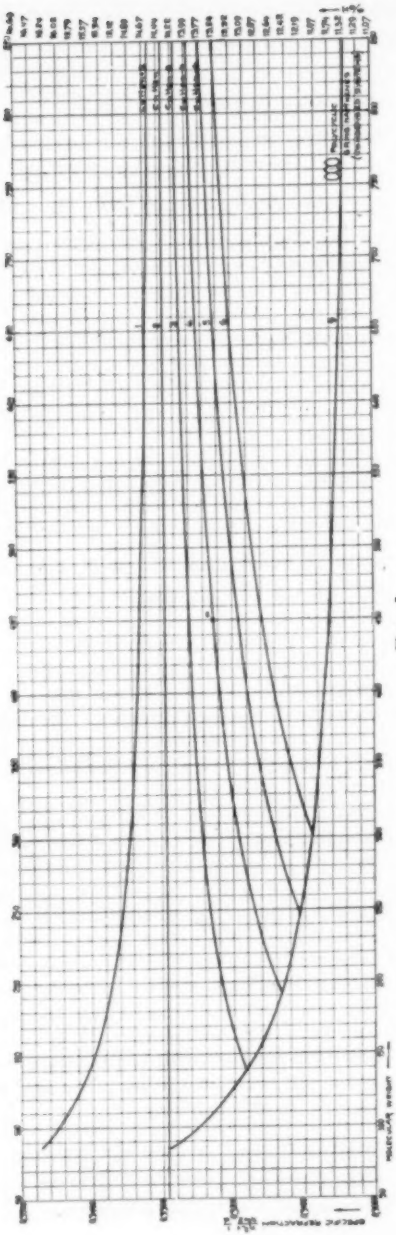

FIG. 1.

the D-line he finds 2·418 for C and 1·100 for H. The molecular refraction $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}$ of saturated hydrocarbons is equal to the sum of the atomic refractions, and consequently the specific refraction $\frac{n^2-1}{n^2+1}\frac{1}{d}$ is equal to the sum of the atomic refractions, divided by the molecular weight. So a saturated hydrocarbon with the composition C_xH_y has a specific refraction $= \frac{x\times 2{\cdot}418 + y\times 1{\cdot}100}{x\times 12{\cdot}0 + y\times 1{\cdot}008}$. All hydrocarbons with the same C/H ratio—that is, with the same hydrogen content—possess the same specific refraction. Therefore, all monocyclic naphthenes (C_nH_{2n}) have the same specific refraction (0·3294). It should be emphasised that the calculation of the specific refraction from the elementary composition is valid only for saturated hydrocarbons, viz. naphthenes and paraffins. For aromatics and olefins the specific refraction calculated from refractive index and density is higher than the value calculated from the atomic refractions. For instance, for naphthalene 0·2576 is calculated from the atomic refractions and from n and d 0·3469 is found.

The saturated oil which in the foregoing served as an example contained 13·59 per cent. H and 86·41 per cent. C. The atomic C/H ratio is therefore $\frac{86{\cdot}41}{12{\cdot}0} : \frac{13{\cdot}59}{1{\cdot}008}$, or 7·201 : 13·482. From this elementary composition, with the aid of Eisenlohr's atomic refractions, the specific refraction is calculated at $\frac{7{\cdot}201\times 2{\cdot}418 + 13{\cdot}482\times 1{\cdot}100}{7{\cdot}201\times 12{\cdot}0 + 13{\cdot}482\times 1{\cdot}008}$ or 0·3225.

In Fig. 1 on the ordinate to the left one finds the corresponding specific refractions, and on the level of point P the value 0·3225. This same value will be calculated from the actual values of n_D^{20} and d_4^{20}.

The Authors have compared specific refractions calculated from n and d to those calculated from the elementary composition for mixtures of saturated hydrocarbons of high as well as of low molecular weight. In all cases very good agreement was observed.

Without difficulty the determination of n_D^{20} and d_4^{20} can be carried out with precision up to the fourth and even to the fifth decimal point, which permits the specific refraction to be calculated with precision up to the fourth decimal point.* Consequently, the Authors are convinced that in most cases the elementary composition of a saturated oil can be derived with more precision from n and d than from the results of the elementary analysis. The oil represented by point P in Fig. 1 may not be homogeneously tricyclic. It might as well be a mixture of equal parts by weight of dicyclic and tetracyclic naphthenes of equal mean molecular weight, and in the extreme case a mixture of paraffins and polycyclic naphthenes without side-chains (so-called 100 per cent. ring naphthenes, curve 9 in Fig. 1). By interpolating between the curve of the paraffins and the curve of the polycyclic naphthenes, the naphthene ring content of P can be found.

* In "Refraktometrisches Hilfsbuch" by Roth and Eisenlohr (1911) a table can be found, which for a large number of values for n gives the logarithm of $\frac{n^2-1}{n^2+2}$. This greatly facilitates the calculation of specific refractions.

The specific refraction of the paraffin with molecular weight 450 amounts to 0·3329, and that of the corresponding polycyclic naphthene to 0·3063, thus giving for P $\frac{0{\cdot}3329 - 0{\cdot}3225}{0{\cdot}3329 - 0{\cdot}3063} 100 = 39$ per cent. naphthene ring and 61 per cent. paraffin.

The ring analysis of paraffin–naphthene mixtures will be concluded with a few examples from practice.

EXAMPLE I.

Mean mol. weight	709
n_D^{20}	1·4754
d_4^{20}	0·8592
$r_D^{20} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$	0·3279

This oil contains on the average 1·7 naphthene ring per molecule. The specific refraction of the paraffin with mol. weight 709 is 0·3314, that of the polycyclic naphthene without side-chains 0·3043. The percentage of naphthene rings in the oil is therefore $\frac{0{\cdot}3314 - 0{\cdot}3279}{0{\cdot}3314 - 0{\cdot}3043} \cdot 100 = 13$ per cent. by weight. So for the paraffinic side-chains and free paraffins there remains 87 per cent. by weight.

EXAMPLE II.

Mean mol. weight	350
n_D^{20}	1·4967
d_4^{20}	0·9194
$r_D^{20} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$	0·3181

The percentage of naphthene rings calculated from Fig. 1 is $\frac{0{\cdot}3337 - 0{\cdot}3181}{0{\cdot}3337 - 0{\cdot}3077} 100 = 60$ per cent., and therefore the oil contains 40 per cent. paraffinic side-chains, eventually free paraffins.

If an oil contains a large amount of solid paraffins, the n_D and d must often be determined at temperatures higher than 20° C. Now, the specific refraction is not altogether independent of temperature, but slightly increases with temperature. For a rise of 20° C. this increase amounts to 0·0005. Fig. 1 is valid for 20° C., and therefore determinations at other temperatures should be corrected.

EXAMPLE III.

Mean mol. weight	371
n_D^{40}	1·4652
d_4^{40}	0·8474
r_D^{40}	0·3263
r_D^{20}	0·3258

The naphthene ring content is then $\frac{0{\cdot}3336 - 0{\cdot}3258}{0{\cdot}3336 - 0{\cdot}3075} 100 = 30$ per cent. and the paraffin content 70 per cent.

Analysis of Oils Containing Aromatic Rings.

Generally, it is desired to analyse oils containing aromatic rings as well as naphthenic rings and paraffins. Only oils which have undergone exhaustive acid treatment may be aromatic free.

To determine the amount of aromatic rings—which rings may occur in one and the same molecule with naphthenic rings and paraffinic side-chains —the Authors hydrogenate these rings quantitatively to hydroaromatic or naphthenic rings. The completely hydrogenated oil is aromatic free, and can therefore be analysed according to the method described above. The aromatic ring content may be calculated from the amount of hydrogen consumed in the hydrogenation of the aromatic rings. A pure aromatic without side-chains consumes on the average 7·8 per cent. by weight of hydrogen during complete hydrogenation.* Suppose a hydrogen consumption of 1·0 per cent. by weight has been found, either from the difference in hydrogen content (elementary analysis) before and after hydrogenation, or from the directly measured volume of hydrogen consumed. Then the aromatic ring content amounts to $\frac{1{\cdot}0}{7{\cdot}8} \times 100 = 12{\cdot}8$ per cent. by weight. However, in this form the method is hardly suitable in practice, as determination of the hydrogen consumption requires much time and great precision. Therefore, instead of the hydrogen consumption the Authors use the rise of the aniline point resulting from the hydrogenation. With a number of hydrogenations the rise of the aniline point has been compared to the actual hydrogen consumption, which gave the result that on the average 1° C. aniline point rise corresponds to 0·85 per cent. by weight of aromatic ring.

Hydrogenation is carried out under high hydrogen pressure in the presence of an active catalyst, viz. nickel on kieselguhr. High temperatures should be avoided, to prevent destruction; in practice, temperature varies from about 200° to 300° C., dependent on the actual rate of hydrogenation. At first the catalyst is often poisoned by sulphur compounds occurring in the oil, but the hydrogenation is then repeated several times with fresh catalyst (after removing the used quantity), until a treatment with hydrogen and fresh catalyst does not give any hydrogen consumption or alteration of the physical constants. This is an indication for complete hydrogenation, but not absolute proof. However, the specific dispersion $\frac{n_{G'} - n_C}{d} 10^4$ is a value which can provide this proof, as will be explained in a following paper. In fact, aromatics have very high dispersion values (about 300), whereas naphthenes and paraffins are low, and both lie between 150 and 158. When, therefore, the specific dispersion $\frac{n_{G'} - n_C}{d} 10^4$ of a hydrogenated oil is below 158, the absence of aromatic rings can be taken for certain. At present, however, determination of this value is no longer necessary, for the aniline point can also demonstrate complete hydrogenation. In Fig. 2 can be found the relation between the aniline point and the specific refraction for paraffin–naphthene mixtures of varying molecular weight. Aromatic

* For benzene this percentage is 7·73, for naphthalene 7·85, for diphenyl 7·83, and for anthracene 7·92.

FIG. 2.

RELATION BETWEEN SPECIFIC REFRACTION AND ANILINE POINT FOR AROMATIC FREE OILS.

hydrocarbons have low aniline points and high specific refractions. During hydrogenation the specific refraction of the oil is lowered and the aniline point is raised; when complete hydrogenation is attained, the aniline point should agree with the value read in Fig. 2.

Before discussing the further significance of Fig. 2, two examples of complete hydrogenation will be given (Tables I and II) to demonstrate how n and d are lowered, and also the specific refraction calculated from these constants, whereas the aniline point is raised until the determined aniline point agrees with the value read in Fig. 2.

TABLE I.

	Original oil.	1st treatment.	2nd treatment.	3rd treatment.	4th treatment.	5th treatment.	6th treatment.	7th treatment.	8th treatment.
Properties.									
Mol. weight	334	—	—	—	—	—	—	—	339
n_D^{20}	1·5251	—	—	1·5171	1·5137	—	1·5019	1·4910	1·4858
d_4^{20}	0·9419	—	—	0·9315	—	—	—	—	0·8932
Spec. refraction	0·3254	—	—	0·3249	—	—	—	—	0·3213
Aniline point (° C.)	62·0	—	—	67·8	—	—	77·0	91·6	94·0
Aniline point (read from Fig. 2)	99·0	—	—	98·4	—	—	—	—	93·8
Sulphur (%)	0·35	—	—	—	—	—	—	—	—
Hydrogenation.									
Reaction temp. (° C.)	—	325	350	340–350	330–340	345–350	340	330	330–340
Reaction time (min.)	—	30	30	20	30	20	30	30	30
Starting pressure (kg./cm.²)	—	115	116	116	118	116	121	118	105
Final pressure (kg./cm.²)	—	112	107	111	114	111	108	102	96

TABLE II.

	Original oil.	1st treatment.	2nd treatment.	3rd treatment.	4th treatment.	5th treatment.
Properties.						
Mol. weight	419	—	—	—	—	417
n_D^{20}	1·5019	—	—	—	1·4848	1·4841
d_4^{20}	0·9089	—	—	—	0·8894	0·8887
Spec. refraction	0·3246	—	—	—	0·3221	0·3220
Aniline point (° C.)	92·2	—	—	97·0	104·5	105·0
Aniline point (read in Fig. 2)	109	—	—	—	105·2	105·0
Sulphur (%)	0·10	—	—	—	—	—
Hydrogenation.						
Reaction temp. (° C.)	—	290	290	340	320–340	300–320
Reaction time (min.)	—	30	30	20	20	20
Starting pressure (kg./cm.²)	—	110	120	125	115	100
Final pressure (kg./cm.²)	—	105	110	105	95	96

After the complete hydrogenation, the molecular weight is determined to ascertain whether any destruction has taken place.

For the oil of Table I the aromatic ring content is $0{\cdot}85 \times (94{\cdot}0 - 62{\cdot}0) = 27$ per cent. by weight. The specific refraction of the completely hydrogenated oil is 0·3213 and the mol. weight 339. Making use of

Fig. 1 or Fig. 2, the percentage of naphthenic rings is calculated at $\frac{0{\cdot}3339 - 0{\cdot}3213}{0{\cdot}3339 - 0{\cdot}3078} \cdot 100 = 48$ per cent. by weight. Of these naphthenic rings 27 per cent. have been formed from aromatics by hydrogenation. Therefore the composition of the original oil is :

27 per cent. aromatic rings,
21 ,, ,, naphthenic rings,
52 ,, ,, paraffinic side-chains.

In the same way, the oil of Table II contains $0{\cdot}85 \times (105{\cdot}0 - 92{\cdot}2) = 11$ per cent. of aromatic rings. The specific refraction of the completely hydrogenated oil is 0·3220, and the mol. weight 417. Interpolating in Fig. 1 or 2, the naphthenic ring content of the aromatic free oil is

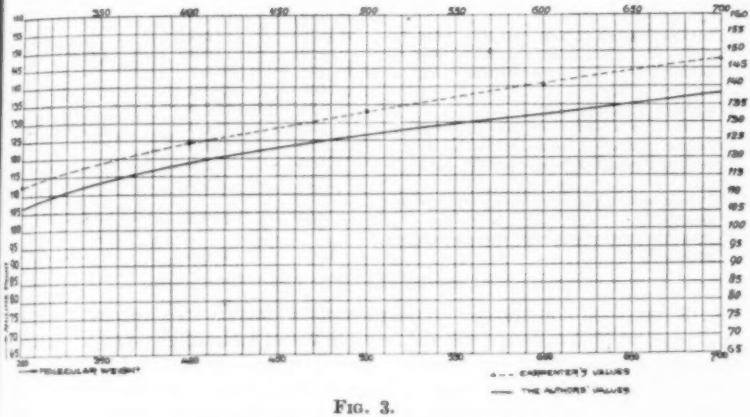

FIG. 3.

ANILINE POINTS OF THE PARAFFINS.

$\frac{0{\cdot}3331 - 0{\cdot}3220}{0{\cdot}3331 - 0{\cdot}3066} \times 100 = 42$ per cent. by weight, of which 11 per cent. have been formed from aromatics. So the composition of the original oil is :

11 per cent. aromatic rings,
31 ,, ,, naphthenic rings,
58 ,, ,, paraffinic side-chains.

Fig. 2. For the construction of this figure the Authors have used the information given by the analysis of about a hundred aromatic free oils. These oils have been prepared from natural oils, not only by complete hydrogenation, but also by exhaustive treatment with sulphuric acid. Furthermore, a number of aromatic free oils have been separated into several fractions by distillation in the cathodic light vacuum.* In the preceding paper, a Fig. 2 has also been given. This figure should, however, no longer be employed, as the aniline points for the paraffins given by

* H. I. Waterman and E. B. Elsbach, *Chemisch Weekblad*, 1929, **26**, 468; H. I. Waterman en J. N. J. Perquin, " Technische Analysen 4e druk," Dordrecht 1931.

Carpenter * were used, which values are probably too high according to our own observations (see Fig. 3 and Table III).

TABLE III.

Aniline Points of Paraffins (compare Fig. 3).

	Mol. weight.	Aniline Point.	
		Author's.	Carpenter's corresponding values.
Fraction from a paraffinic gas oil	224	94·2° C.	—
Hexadecane	226	94·7	99·5° C.
Fraction from a paraffinic gas oil	236	96·1	—
" " " "	246	98·1	—
" " " "	289	105·0	—
Fraction from Rangoon paraffin wax	372	114·6	—
Paraffin prepared from Carnauba wax	372	116·0	123·0
Fraction from Rangoon paraffin wax	395	118·7	—
" " " "	409	120·0	—
Rangoon paraffin wax	425	121·0	—
Fraction from Rangoon paraffin wax	430	121·0	127·0
Fraction prepared from Carnauba wax	440	121·5	—
Fraction from Rangoon paraffin wax	466	123·5	—
" " " "	475	124·6	—
Polymerisation product of cetene (hydrogenated)	550	129·5	—
Polymerisation product of cetene (hydrogenated)	1020	156·0	—

Fig. 2 has been constructed by connecting aromatic free oils with equal aniline point (but different specific refraction and mol. weight, and therefore different composition) by curves. Among these aromatic free oils are narrow fractions and oils with a large boiling range, and therefore this figure may be used for all kinds of paraffin–naphthene mixtures. Physical

TABLE IV.

Properties of Mixtures of Hydrogenated Oils.

	Mol. weight.	$n_D^{20°}$.	$d_4^{20°}$.	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ at 20° C.	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ calculated for mixture.	Aniline point ° C.	
						Found.	Read in Fig. 2.
Oil I	405	1·4815	0·8813	0·3232	—	105·4	105·3
Oil II–fraction VI	410	1·5010	0·9267	0·3179	—	96·0	97·9
Mixture 1 : 1 by weight	407	1·4911	0·9033	0·3207	0·3206	100·4	101·7
Oil II–fraction IV	354	1·5011	0·9282	0·3175	—	88·2	90·4
Oil III–fraction II	368	1·4724	0·8592	0·3262	—	105·2	105·2
Mixture 1 : 1 by weight	361	1·4865	0·8921	0·3221	0·3219	97·4	97·8
Oil II–fraction VII	451	1·4887 $^{40°}$	0·9011 $^{40°}$	0·3206	—	105·3	105·7
Oil II–SO_3-raffinate	362	1·4948	0·9145	0·3188	—	91·0	93·5
Mixture 1 : 1 by weight	402	1·4924 $^{40°}$	0·9084 $^{40°}$	0·3198	0·3197	99·6	99·9
Oil III–fraction II	368	1·4724	0·8592	0·3262	—	105·2	105·2
Oil II–SO_3-raffinate	362	1·4948	0·9145	0·3188	—	91·0	93·5
Mixture 1 : 1 by weight	365	1·4833	0·8861	0·3225	0·3225	99·8	99·4

* *J.I.P.T.*, 1928, **14**, 461.

constants of some narrow fractions, complete oils, and mixtures (all aromatic free) are given in Table IV.

It has already been stated that when an oil still contains aromatic rings, the aniline point cannot be the same as read from Fig. 2. The larger the difference, the larger the percentage of aromatic rings present. For instance, the following constants are found for an oil rich in rings: mol. weight 362, aniline point 63·0° C., specific refraction (from n and d) 0·3239. According to Fig. 2, the aniline point corresponding to a specific refraction of 0·3239 and a molecular weight of 362 is not 63·0° C., but 100·9° C., the difference being 37·9° C. It is possible to deduce from this difference to what extent the aniline point will rise and the specific refraction drop if a complete hydrogenation were carried out. Of course, this is a very important application of Fig. 2, for now hydrogenation becomes superfluous. As a matter of fact, the Authors have found that 0·80 × this difference equals the predicted rise of the aniline point. In this instance the predicted rise of the aniline point is 0·80 × 37·9 = 30·3° C., and the expected aniline point of the completely hydrogenated oil 93·3° C. (found 94·4° C.). Now also the specific refraction of the completely hydrogenated oil can be predicted, since with an aniline point of 93·3° C. and a molecular weight of 362 we read in Fig. 2 0·3187 (found 0·3188).

By a correct combination of the constants (mol. weight, aniline point, n_D^{20} and d_4^{20}) of the original oil the chemical composition can therefore be found.

As an example, the complete analysis of a paraffin base oil (Pennsylvanian type) and of a naphthene base oil, rich in rings, will now be given.

Pennsylvania Lubricating Oil.

The original oil has the following properties:

Mol. weight	512
n_D^{20}	1·4877
d_4^{20}	0·8760
r_D^{20}	0·3287
A.P.	111·8° C.

After complete hydrogenation the constants are:

Mol. weight	511
n_D^{20}	1·4750
d_4^{20}	0·8632
r_D^{20}	0·3262
A.P.	121·0° C.

This oil contains on the average 2·0 ring per molecule (see Fig. 1). Hydrogenation has caused the aniline point to be raised 9·2° C., so the original oil contains 9·2 × 0·85 = 8 per cent. by weight of aromatic rings. After hydrogenation the specific refraction is 0·3262, so that the hydrogenated oil contains $\frac{0{\cdot}3323 - 0{\cdot}3262}{0{\cdot}3323 - 0{\cdot}3057} \times 100 = 23$ per cent. by weight of naphthenic rings, of which 8 per cent. have been formed from aromatic rings. The original Penna oil therefore consists of:

8 per cent. of aromatic rings,
15 ,, ,, of naphthenic rings,
77 ,, ,, of paraffinic side-chains.

The properties of the hydrogenated oil may be predicted from those of the original oil as follows. In Fig. 2, at a specific refraction of 0·3287 and a molecular weight of 512, an aniline point of 122·3° C. is read. The difference between A.P. found and A.P. read is 10·5° C. The predicted A.P. rise is therefore $0{\cdot}80 \times 10{\cdot}5 = 8{\cdot}4°$ C., and the predicted aniline point of the hydrogenated oil 120·2° C. (found 121·0° C.). This aniline point corresponds to a specific refraction 0·3270 (found 0·3262), from which the naphthene ring content is calculated at $\frac{0{\cdot}3323 - 0{\cdot}3270}{0{\cdot}3323 - 0{\cdot}3057} \times 100 = 20$ per cent. by weight. Of this 20 per cent. $0{\cdot}85 \times 8{\cdot}4 = 7$ per cent. would have been formed from aromatic rings. In this way from the constants molecular weight, n_D^{20}, d_4^{20} and aniline point the composition of this Penna oil is deduced at :

7 per cent. aromatic rings,
13 ,, ,, naphthenic rings,
80 ,, ,, paraffinic side-chains.

As this high molecular oil is liquid at room temperature, and therefore contains no or very little normal free paraffins, the paraffinic part of the oil will be principally present as paraffinic side-chains.

Naphthene Base Oil.

The constants of the original oil are :

Mol. weight	349
n_D^{20}	1·5420
d_4^{20}	0·9690
r_D^{20}	0·3248
A.P.	52·6° C.

After complete hydrogenation these constants are :

Mol. weight	352
n_D^{20}	1·4989
d_4^{20}	0·9235
r_D^{20}	0·3179
A.P.	90·4° C.

The oil contains on the average 3·6 ring per molecule. The aniline point has risen 37·8° C., from which the aromatic ring content is calculated at $0{\cdot}85 \times 37{\cdot}8 = 32$ per cent. by weight. The hydrogenated oil contains $\frac{0{\cdot}3337 - 0{\cdot}3179}{0{\cdot}3337 - 0{\cdot}3077} \times 100 = 61$ per cent. by weight of naphthenic rings and 39 per cent. by weight of paraffins. The complete analysis of the original oil is therefore :

32 per cent. aromatic rings,
29 ,, ,, naphthenic rings,
39 ,, ,, paraffinic side-chains.

Deduction of the composition without carrying out the hydrogenation takes place as follows. An aromatic free oil with molecular weight 349 and specific refraction 0·3248 should have an aniline point of 100·3° C. (Fig. 2).

There is found 52·6° C., the difference being 47·7° C. The predicted A.P. rise on complete hydrogenation is therefore $47{\cdot}7 \times 0{\cdot}80 = 38{\cdot}2°$ C., the predicted A.P. 90·8° C. (found 90·4° C.) and the predicted specific refraction 0·3183 (found 0·3179), from which the naphthenic ring content of the hydrogenated oil is calculated at $\frac{0{\cdot}3337 - 0{\cdot}3183}{0{\cdot}3337 - 0{\cdot}3077} \times 100 = 59$ per cent. by weight. Thus the original oil contains :

32 per cent. of aromatic rings,
27 ,, ,, of naphthenic rings,
41 ,, ,, of paraffinic side-chains.

Carrying Out a Determination.

Of an unknown oil the density (d_4^{20}), the index of refraction (n_D^{20}), the aniline point (A.P.), and the mean molecular weight (M.W.) are determined.

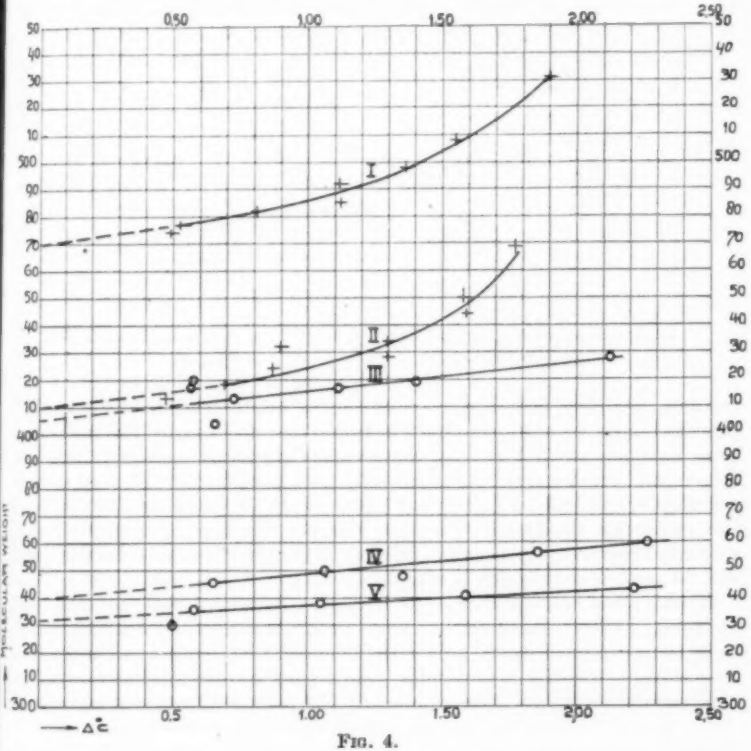

Fig. 4.

INFLUENCE OF THE CONCENTRATION ON THE MOLECULAR WEIGHT IN NAPHTHALENE.

The *density* is determined by means of a Sprengel pycnometer, the *index of refraction* by means of the Abbé refractometer. These constants must be

known *accurately to the fourth decimal point*, so as to enable us to calculate also the specific refraction accurately to four decimal points, because the specific refraction of aromatic free oils in the range of lubricating oils varies from about 0·3300 (oils rich in paraffins) to 0·3180 (oils rich in rings).

The temperature at which *equal volumes* of oil and dry aniline become turbid on cooling is called the aniline point. The so-called maximum aniline points still give rise to confusion, and for this reason the fact is emphasised that the volumes are to be equal.

For determining the *molecular weight*, the Authors apply the cryoscopic method in naphthalene or benzene. The procedure is always such that depression of the freezing-point in naphthalene is 1·0° C. and in benzene 0·75° C. As a matter of fact, the concentration of the oil is then about the same for both solvents, the molecular lowering of the freezing-point of naphthalene being 69·3 and that of benzene 51·2. It should be noted that in this manner one does not find the perfectly correct molecular weight, since this would necessitate several determinations at different concen-

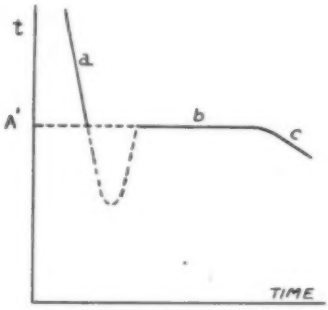

FIG. 5a.

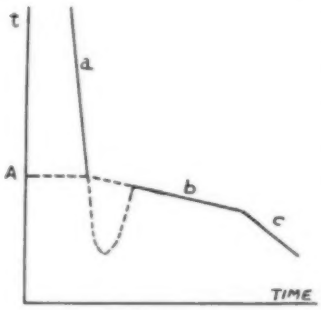

FIG. 5b.

trations, enabling one to extrapolate for a concentration of zero. For practical purposes this manipulation would take too long. The investigations have shown that in most cases values are found approximating the correct molecular weight, and that only with paraffins or oils very rich in paraffins are the values slightly too high. In Fig. 4, showing the change of the molecular weight with the depression of the freezing-point of naphthalene, I represents a paraffin base oil, II is Rangoon paraffin wax, and III, IV, and V are oils rich in rings.

Naphthalene has a particular advantage. As a matter of fact, the high molecular hydrocarbon mixtures may contain free normal paraffins, which in benzene can be dissolved only with difficulty. In this case, with benzene as a solvent, too high a molecular weight may be found, when on cooling solid paraffins separate before the solidifying-point of the solvent is reached. As for the rest, benzene as well as naphthalene may be used as is shown by Table V.

Further, the temperature–time curve is particularly important in regard to the determination of the molecular weight.* A pure substance such as

* N. G. Gullick, *J.I.P.T.*, 1931, **17**, 541.

naphthalene has a definite point of solidification (Fig. 5*a*), but with a mixture of oil and naphthalene the temperature falls when naphthalene crystallises out (Fig. 5*b*). Therefore the point of intersection of the lines *a* and *b* indicates the correct freezing-point. Consequently the depression of the freezing-point is $A' - A$.

For determining the molecular weight in naphthalene, the Authors use a small flask closed by a thermometer. Naphthalene and oil are weighed into this flask, the mixture is molten over a small flame, and the flask is then shaken by hand in a wide test-tube, which is kept at 78° C. by a water-bath. It is not advisable to use a thermometer with a very thin thread of mercury. In practice a thermometer divided in 0·05° C. gives good results.

With the apparatus described, a determination can be carried out within half an hour. After the determining of d_4^{20}, n_D^{20}, molecular weight and aniline point, the oil is subjected to a pressure hydrogenation. The starting pressure is 100–120 kg./cm.^{2}, temperature 250–300° C. (maximum 350° C.), the catalyst consists of finely divided nickel on kieselguhr. When the oil is free from sulphur, hydrogenation proceeds very fast under these conditions, but in most cases hydrogenation should be repeated several times with fresh catalyst. The used catalyst should be removed, which can best be done by washing the oil out of the autoclave with benzene, filtering by suction, and driving the benzene off in a vacuum. One or more of the constants of the oil are determined, and then with fresh catalyst hydrogenation is repeated. When hydrogen is no longer absorbed and the constants no longer change, the oil is completely hydrogenated. This may be controlled by the aniline point and by dispersion values (to be dealt with in a later paper).

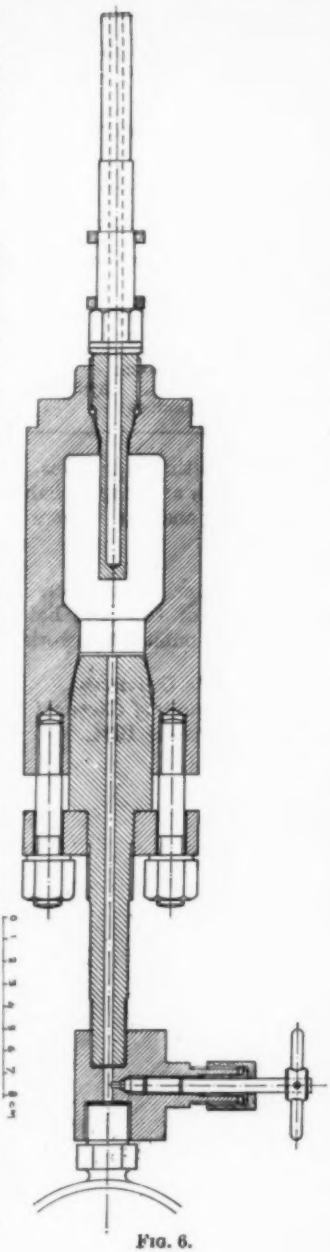

FIG. 6.

For recent experiments the Authors

TABLE V.

Molecular Weights in Benzene and Naphthalene.

Hydrocarbon oil.	Cryoscopic molecular weight with as a solvent	
	benzene.	naphthalene.
Polymerisation product	881,876	868,878
„ „ completely hydrogenated	878	883
Perhydroanthracene	196	192
Completely hydrogenated lubricating oil	354	350
Kerosene	195	200
Diesel oil	234	230
Completely hydrogenated Diesel oil	232	233
Oils separating solid paraffin on cooling :		
Polymerisation product	1451	1230
„ „ hydrogenated	1621	1360
Condensation product	811	753

use small rotating autoclaves, as shown in Fig. 6, with a volume of about 130 ml., which are easy to handle and require only 30 ml. of oil for the complete ring analysis. The working pressure is 250 kg./cm.^{2}, temperature max. 400° C.

In conclusion, the Authors wish to communicate their thanks to the Management of the N.V. Bataafsche Petroleum Maatschappij for kind permission to publish this work.

Delft, The University,
Laboratory of Chemical Engineering.
October 1934.